

Energy Material, Chemical Engineering and Mining Engineering

Edited by
B. Xu and H.Y. Li



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Edited by

B. Xu and H.Y. Li



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Preface

2012 International conference on Energy Material, Chemical Engineering and Mining Engineering (EMCEM2012) is a conference focusing its center on Energy Material, Chemical Engineering and Mining Engineering. The objective of the conference is to provide a forum for different researchers in different fields especially in Material field to exchange their different findings. The researchers are from different countries and in different professionals. The conference will bring all the researchers from all around the world together to share their new findings, thus to promote academic exchanging.

All the papers accepted had been passed the strict peer-review course before their publication by TTP. Here, we should show our sincere thanks to all authors for their high-quality papers and their careful presentations in the conference. At the same time, all reviewers should be thanked too for their careful work. In addition, all sponsors and all team members of TTP should be especially thanked too for their hard work and careful edition on EMCEM2012.

It's the joint efforts of all different parts that they makes our conference be successful.

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CHAPTER 1:

Energy Materials and Material Applications with Analysis of Material Properties

Study on Biomass Energy Materials---Briquetting Fuel and Its Applications in Power Generation

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Keywords: Biomass; Energy materials; Briquetting fuel technology; Power generation technology

Abstract. Biomass is an important energy material, which can be used for power generation in large scale after briquetting. In the paper, the briquetting methods such as biomass cold briquetting, thermal briquetting and common briquetting as well as biomass briquetting machines of ring die, flat die, piston and screw type were firstly presented. Combined with biomass briquetting fuel technology and biomass power generation technology, the characteristics of biomass briquetting fuel direct combustion power generation, co-firing power generation and gasification and power generation technologies were elaborated. Finally, there was an outlook for the development prospect of such energy materials and its power generation technology in China. A conclusion to their economic, environmental and social benefits were gotten, which provides a certain reference for comprehensive application of biomass resource with high efficiency.

Introduction

As the only renewable energy available to store, transport and fix carbon, biomass energy is characterized by its large storability, wide distribution, environment-friendly and low carbon and almost zero emission and so on and plays as vital part in the six renewable energies. Usually, the raw material of biomass energy contains agricultural residues, forestry residues, animal manure, energy crop (plant), industrial organic wastewater, city domestic sewage and rubbish, etc. This energy provides almost 15% of the total energy consumption of the world, becoming the fourth largest energy right next to petrol, coal and natural gas.

China is of rich biomass resources, of which agricultural and forestry residues comprise a great proportion. However, biomass such as agricultural and forestry residues are of dispersed resources, low energy density, small bulk weight and are inconvenient for storage and transportation, which badly limit their application to a large scale. By taking briquetting fuel technology, the dispersed raw materials (mainly in agricultural and forestry residues) with uncertain shapes can be compressed into briquetting fuels with a certain geometry and lager density through processes of drying, chopping and briquetting, etc. Briquetting fuel increases the density of biomass, saves expenditures on transportation and storage, enlarges energy application range, improves combustion efficiency and reduces environmental pollution caused by the replaced coal combustion at the same time [1-6]. Meanwhile, biomass power generation technology is the currently most mature technology on application of modern biomass energy with the largest developing scale in the world, mainly including biomass direct combustion power generation, co-firing power generation and gasification power generation, and biomass briquetting fuel power generation has become one of the key developing directions in that of biomass power generation technology.

In the paper, biomass cold briquetting, thermal briquetting and common briquetting were presented. Biomass briquetting machines of ring die, flat die, piston and screw type were described. On the base of biomass briquetting fuel technology and biomass power generation technology, the characteristics of three kinds of biomass briquetting fuel power generation were elaborated. The development prospect of biomass briquetting fuel and its power generation technology in China was gotten with their economic, environmental and social benefits, which can provide some data for utilization of biomass resources.

Briquetting fuel technology

Biomass, such as agricultural and forestry residues, are mainly composed of cellulose, hemicellulose and lignose, where lignose is a natural polymer produced through photosynthesis, with complex three-dimensional structure, belonging to polymer substance and accounting for 15% to 30% in content of plant. When temperature reaches 70 to 100°C, lignose begins to soften with certain viscosity; when temperature is up to 300°C, it is melted with high viscosity. At this time, an application of certain external force to it can closely stick it with cellulose, greatly minify the plant volume and increase the plants' density; owing to involvement among inelastic fiber molecule, the given shape can be kept still after withdrawing of external force and the strength would be further increased after cooling. After briquetting, the volume of biomass raw material will be densified, density within 0.7 to 1.4t/m³ and percentage of moisture under 20% in general.

In the processing principle, biomass briquetting can be divided into cold briquetting, thermal briquetting and common briquetting [7,8]: (1) For biomass cold briquetting, namely a process to compress biomass granule into shape with high pressure under normal temperature, the plasticizing bonding of lignose in biomass is mainly with the aid of heat produced in the process of compacting. (2) For thermal briquetting, namely hot compacting, the process flow includes raw material chopping, drying mixing, extrusion forming and cooling for package. According to different heating positions for raw material, heating action to raw material can be divided into two kinds, i.e. heating at briquetting position only and heating respectively before putting raw materials into compressing mechanism and at briquetting position. (3) For common briquetting, namely forming under normal temperature and moisture condition, after corruption to a certain extent, fiber comes to be soft, wet, cracking and partly degraded, at which time it is easy to be briquetted; then extrude water out from the partly degraded agricultural and forestry residues with a simple die, thus the briquetting fuel can be got. In processing flow, biomass briquetting technology generally contains drying, chopping and briquetting, etc. [9]. The main flow is as shown in Fig.1.

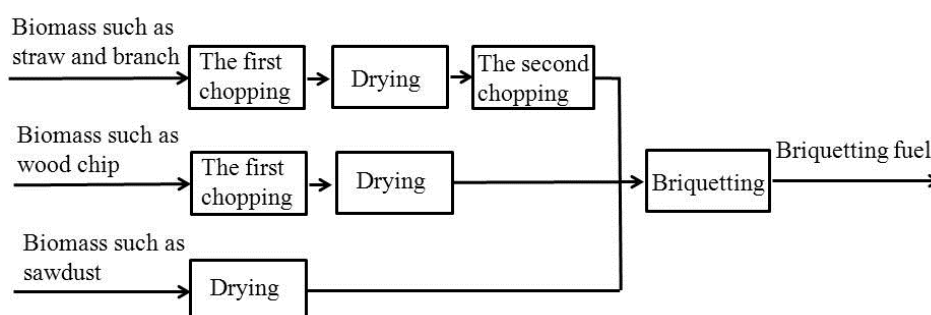


Fig.1 Flow chart of biomass briquetting fuel system

Briquetting fuels are respectively processed into various shapes with equipment that adopted briquetting principles such as screw extrusion, piston stamping and die stamping, etc., where granular fuel is mostly produced by die briquetting equipment including flat die briquetting and ring die briquetting; while bar or block shaped briquetting fuels can be processed by those three briquetting equipment. Currently, there are four kinds of biomass briquetting machines with ring die, flat die, piston and screw respectively, see Fig. 2 for working principles of each briquetting machine.

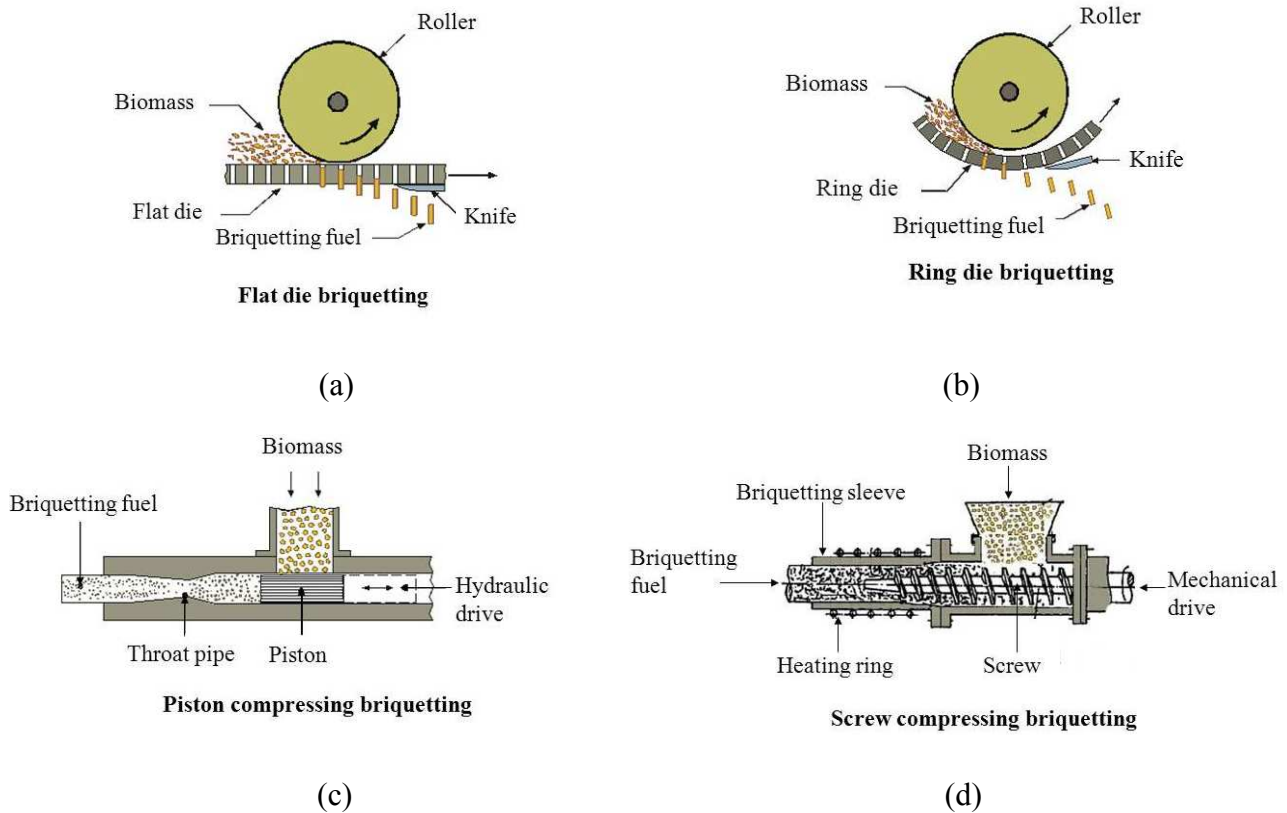


Fig.2 Schematic diagram of biomass briquetting fuel machine

Briquetting fuel power generation technologies

Biomass briquetting fuel power generation technology, integrated briquetting fuel technology with biomass power generation technology, is under the support of *Renewable Energy Law* of PRC for development and also enjoys priority in the international scientific and technological cooperative planning of the Ministry of Science and Technology of PRC for renewable energy and new energy resource. Biomass briquetting fuel can be used for biomass direct combustion power generation, co-firing power generation and gasification and power generation [10-12]. The application of biomass briquetting fuel to power generation can be formed into a set of automatic, industrialized biomass briquetting fuel system integrated processes of biomass drying, chopping and briquetting, with guarantee for stable, reliable and economic operation of the whole set of equipment; in this way, the produced biomass briquetting fuel is of density, granular size and combustion performance indexes that are close to that of coal and of good adaptability to combustion equipment (e.g. boiler) and gasification equipment (e.g. gasifier); at the same time, a stable supply of biomass power generation fuel can be guaranteed by establishing and perfecting a collection, storage and processing system for biomass raw material to form a continuous, stable briquetting operation mode.

Biomass Briquetting Fuel Direct Combustion Power Generation. Biomass briquetting fuel direct combustion power generation mainly refers to circulating fluidized bed combustion power generation (see Fig.3): generating power through combustion of biomass briquetting fuel, instead of coal, in circulating fluidized bed boiler reconstructed technically in accordance with combustion characteristics of biomass briquetting fuel based on the existing small thermal power plant, with biomass fuel briquetting technology and equipment; solve issues on corrosion to heat exchanger by the clogging and alkali metal produced in combustion of biomass by reconstructing the fluidized bed boiler with its proper operational processing parameters according to the combustion and fluidization performance of biomass briquetting fuel; and reasonably adjust the air input proportion

of primary air and secondary air. By reason that the power is generated by co-combustion of biomass briquetting fuel and coal with equipment reconstructed on the basis of the original equipment of small thermal power plant, this method is characterized by less investment and lower technical requirement, which is available to prevent small thermal power plant from being shut down.

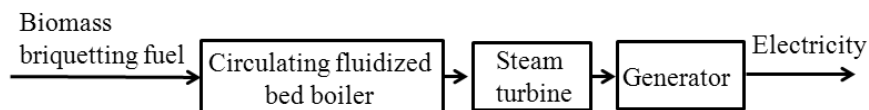


Fig.3 Flow chart of biomass briquetting fuel direct combustion power generation

Biomass Briquetting Fuel Co-firing Power Generation. Biomass is close to coal in physical and chemical performances the most among is renewable energies, therefore, power generated by co-firing of biomass briquetting fuel (with mixing proportion up to 80% theoretically) and coal both utilizes biomass resources reasonably and reduces pollution caused by coal combustion. Meanwhile, this power generation technology (see Fig.4) not only solves issue on the non-renewable property and shortage of conventional energy but also overcomes the unstable operation of power plant caused by seasonal variation of biomass resource. In addition, this technology is of good economic efficiency, flexible scales and can makes full use of the original equipment and system of coal fired power plant; and power plant can be kept in normal operation by adjusting the mixing proportion of biomass for combustion and risk on raw material supply according to richness degree of biomass resources. This technology can be applied to all industries that adopt circulating fluidized bed boiler, e.g. power plant and industrial boiler, etc. When co-firing with coal of low heating value, the thermal utilization factor of boiler can be increased by around 10%, discharge of SO₂ reduced by above 50% and discharge of NO_x reduced by above 30%, in comparison with that of coal combustion.

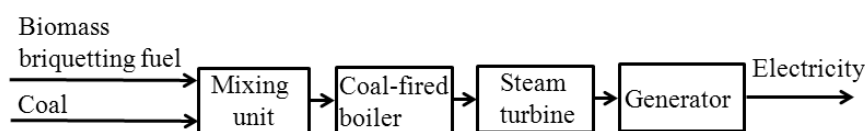


Fig.4 Flow chart of biomass briquetting fuel co-firing power generation

Biomass Briquetting Fuel Gasification Power Generation. Targeting at environmental pollution caused by combustion of biomass straw on site and coking caused in the process of biomass briquetting power generation and co-firing power generation, it has been a key developing direction in biomass energy utilization to R&D and promote biomass briquetting fuel gasification and power generation technology which is technically flexible, environmental-friendly, clean, economical and practical and high-efficiency. Power generated in this technology goes through a combined cycle processing line from biomass gasification to gas engine power generation and then waste heat steam turbine power generation (see Fig.5), which avoids the process with high requirement for gas purification under high temperature, significantly reduces the technical difficulty and construction cost of the whole biomass gasification combined cycle system, solves issues on tar oil and secondary pollution with lower cost and realizes recycling of waste water [13]. Gas produced by gasification of biomass with low heating value can meet the requirement of internal gas-combustion generator, however there is limitation in its max. input power that can be achieved; and the waste gas discharged from biomass gasification power generation system is able to meet the requirement for environmental protection, meanwhile gasification and power generation unit shall be well matched with biomass gasification unit.

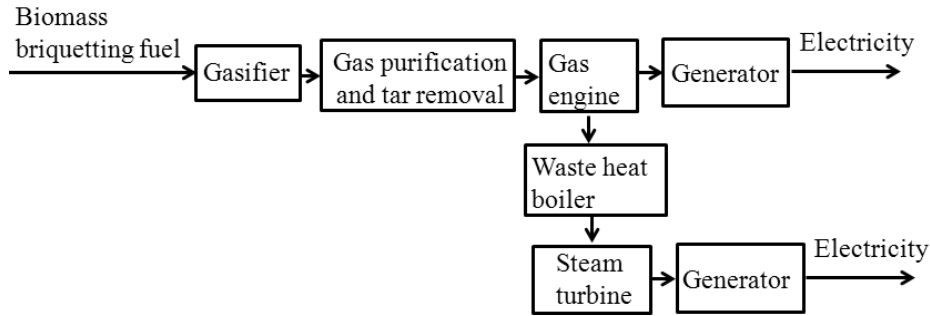


Fig.5 Flow chart of biomass briquetting fuel gasification and power generation

Development prospect of briquetting fuel power generation in China

In confronting with exhaustion of energy resources and pollution caused by using it, making energy structural adjustment and actively developing and utilizing new energy and renewable energy has become an important way to realize sustainable development of energy. As biomass resource is renewable with lower pollution emission, biomass power generation has been widely concerned in Euro-American countries and Japan [14], etc. China is a country of very rich biomass resources, where the annual output of only agricultural residues reaches 0.7 billion ton, among which 0.3 to 0.4 billion ton (equivalent to 150 to 200 million ton normative coal) can be used as fuel; the annual output of forestry residues that can be used as fuel is 0.2 to 0.3 billion ton (equivalent to 100 to 150 million ton normative coal); totally, the usable amount of agricultural and forestry residues can be converted into approximately 350million ton normative coal, which is equivalent to 1/6 of the annual output of raw coal in China. As is stated in the *Mid-Long term Development Plan for Renewable Energy* issued by the national Development and Reformation Commission of China in September, 2007, biomass solid briquetting fuel and biomass power generation are listed as the key development field and it is clearly stated that the usable amount of biomass briquetting fuel shall reach 50 million ton and the installed gross capacity of biomass power generation shall be up to 24 million kW in 2020 [15]. Meanwhile, the popularization and implementation of biomass briquetting fuel power generation technology is one of the vital insurance for realizing the goals in biomass briquetting fuel and biomass power generation. It is of great significance for increasing income of farmers, beautifying rural environment and reducing primary energy consumption and pollution, with great benefits to economy, environment and society.

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Summary

In rational combination of biomass briquetting fuel technology and biomass power generation technology, biomass briquetting fuel power generation is of predominant economic, environmental and social benefits and is of great significance for reducing energy consumption, improving energy structure, lower environmental pollution, rational utilization of resources and increasing income of farmers, etc.

Economically, the application of biomass briquetting fuel power generation technology can make electric power less dependent on fossil fuel and the use of biomass resources such as agricultural and forestry residues with lower cost as raw materials for power generation saves fossil fuel energy such as coal; meanwhile, the reconstruction cost of mid-small sized power plants can also be decreased by taking such technology.

Environmentally, biomass briquetting fuel is renewable with low sulfur, which directly or indirectly lessens the pollution caused by fossil fuel in process of power generation to be converted into electric power

Socially, biomass briquetting fuel power generation technology overcomes the disadvantages of biomass (e.g. agricultural and forestry residues) such as dispersal, low density and inconvenience to store and transport, makes such energy available to be used to a large extent, avoids random incineration of biomass resources and increases income of its local farmers at the same time; additionally, mid-small sized power system such as briquetting fuel power generation covers the shortage of large power grid in security and stableness, which is a complementation to the large-scale power generation system.

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Finite Element Analysis of Energy Saving Jointing Method Base on Energy Materials: Clinching

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Keywords: Clinching, Finite Element Analysis, Segmented Die, Energy Saving

Abstract: The clinch joining technique can be used to join energy saving materials based on a cost effective, environmentally friendly process. In this paper, the mechanical joining method by clinching with segmented die is analyzed utilizing a finite element method. A comparison is conducted about the principle of forming process and the metal flowing direction for two different types of die, drawing conclusions that a better interlocking length can be obtained using segmented die. Analyzing the quality parameter of the clinching results, finds the reason why the segmented die can get a better neck thickness and undercut. Meanwhile, the results of clinching with segmented die also show a good agreement with experimental results.

1. Introduction

The use of energy materials such as aluminium alloys and magnalium has increased in the current automotive manufacturing practice for energy saving and in terms of environmental protection. But some new energy materials cannot be joined by the spot welding or some traditional screws. An alternative method called clinch will become an important joining technique in the next generation of automobile manufacturing, because of its advantages that traditional joining methods such as welding don't have. The clinching process is an alternative joint method of joining sheet metal by localized cold-forming of the materials, which is shown in Fig.1. This produces an interlocking friction joint between two or more layers of material. Comparing to the welding process, clinching offers tremendous improvements in terms of environment protection. For instance, electrical energy consumption reduced by 10 to 20 times, no toxic fumes, no sparks, low noise, no need for refrigeration energy and so on.

There are two different types of clinching die called segmented die and integrate die respectively (Fig.2). The segmented die comprises a basic die body and individual die segments, which are held in position by a steel spring. A surrounding cage permanently secures the separate sections to the die body preventing them from falling out. The die cavity can be formed by 2, 3 or 4 segments with die designs being selected depending on the application requirements.

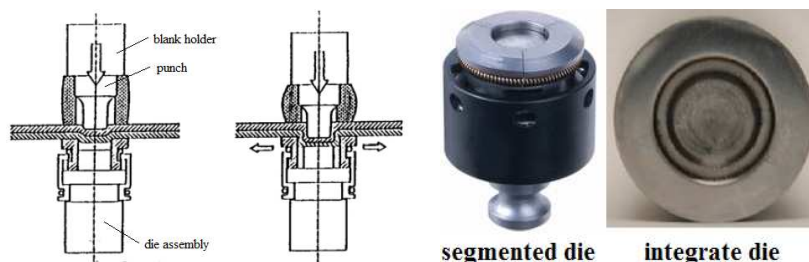


Fig.1 The principle of clinching

Fig.2 The die of clinching

X. He[1] has reviewed the development of clinching in terms of process, strength, and vibration characteristics, by means of finite elements analysis. A finite element simulation has been established by Mosheng Feng[2] for analyzing the forming process and the variation tendency of stress-strain along with time. Hamel et al.[3] has developed a finite element procedure with automatic remeshing technique to specifically simulate the clinch forming process. The effects of tools geometry on both the nick thickness and the clinch lock were studied by A.A.de Paula[4], by making some geometry modifications.

These works, however, are not exhaustive and almost all simulations are carried out with integrate die. Few scholars propose a process simulation with segmented die which is used more extensively in practical application, owing to a series of problems on model establishing, grid technique adopting, and parameters setting. The aim of this study is to simulate the principle of forming and the process of clinched joint to analyze the superiority of segmented die.

2. Finite element analysis of clinched joint with segmented die

2.1. Finite element model

The schematic of the initial geometry used to investigate the clinch forming process is shown in Fig.3; all dimensions are in millimeter(mm). And also the dimensions of punch and die of finite element model are the same as the practical geometry. The sheets are made of aluminium alloy 5052 with 2mm thickness each. The material properties are tabulated in Table 1:

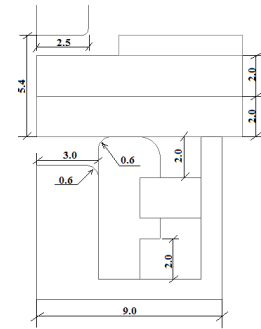


Fig.3. Basic geometry for the simulation of clinching

Table 1 Material properties

Material designation	Density (kg/m ³)	Young's modulus (GPa)	Poisson's ratio	Yield strength (Pa)	Shear modulus(Pa)
AL-5052	2750	70	0.33	1.2*10 ⁸	3.84*10 ⁸
Elastic material	4982.382		0.499		
Rigid material	7850	200	0.3		

The simulation of clinched process with segmented die is carried out using an axisymmetric model which allows its representation by only half of the tooling with a dynamic explicit software of ANSYS/LS-DYNA. The piecewise-linear plasticity material model which adopt Cowper-Symbols model to consider the influence of strain rate is used. It can be used to analyze a series of plastic hardened metallic material. The relationship between the Cowper-Symbols model and yield stress is in follow:

$$\sigma_y = \left[1 + \left(\frac{\dot{\epsilon}_t}{C} \right)^{\frac{1}{P}} \right] (\sigma_0 + f(\epsilon_{eff}^P)) \quad (1)$$

Where σ_0 is the yield stress in constant strain rate; $\dot{\epsilon}_t$ is the effective strain rate; C and P are the parameters of strain rate; $f(\epsilon_{eff}^P)$ is the hardening coefficient which is base on the effective plastic strain.

Since the performances of the spring are similar with the rubber, Mooney-Rivlin elastic rubber model is used to substitute the spring. Whereas the punch die and blank holder are treated as rigid. The material properties of them are presented in Table 1.

All geometrical models are meshed using the plane element 2D Solid162, involving 5427 elements with 5905 nodes in the mesh in all. The finite element model is illustrated in Fig.4(a).

The clinching application involves a large deformation with high local plastic strains in sheets, resulting in severe local mesh distortions. For this reason, the ALE adaptive technique in ANSYS/LS-DYNA is used. ASS2D single contact is conducted to judge the contacts that act between the surfaces by software itself, and the Coulomb friction model is accepted for all contacts surface with a static friction coefficient $\mu=0.1$ and dynamic friction coefficient $\mu=0.2$. The force on the punch is defined as displacement-time curve, and on the blank holder as force-time curve. The clinch time defined as 1.2 second in accordance with the practical time.

2.2. Results

The whole process is divided into three parts on an average which are displayed in Fig.4. It can be seen that aluminium alloy sheets flow into the lower die with the punch stamping. At the same time, the separate sections of the segmented die stretch in order to make the metal sheets deformed as sufficiently as possible, until the sheets formed a clinched joint.

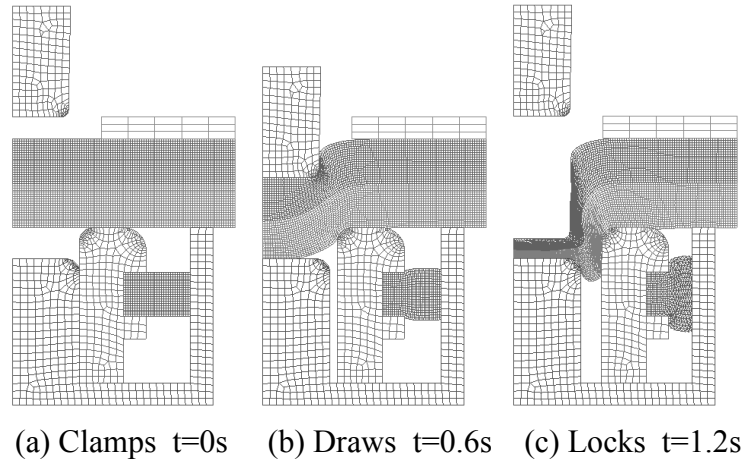


Fig.4 Simulation result of segmented die

Fig.5 displays the sheets cross-section in the area of their connection, including the main quality parameters. The characteristics results of experimental test and simulating with two different types of die are demonstrated in Table 2. A conclusion can be drawn that using segmented die to clinch can accept a better neck thickness and undercut than integrate die. That is to say, clinching with segmented die can get a better joint quality. Moreover, both Fig.5 and Table 2 show a good agreement between simulation and experimental results of clinching process with segmented die.

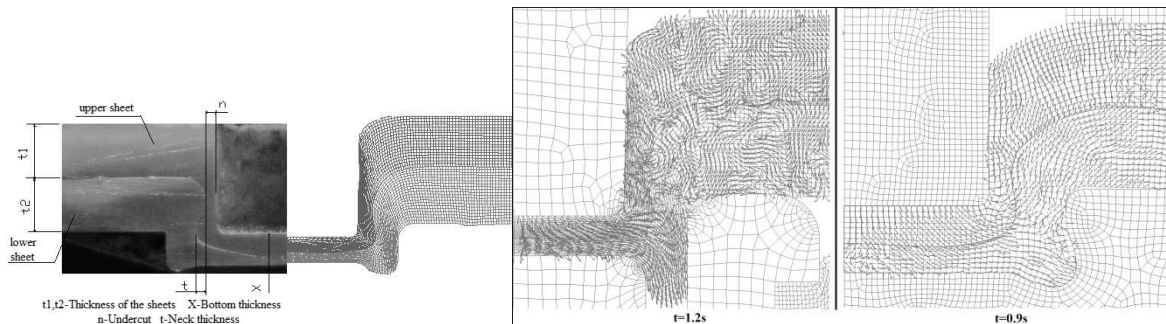


Fig.5 Experimental and simulation result of segmented die

Fig.6 Metal flowing direction in two types of dies

Table 2 Results of the quality parameters

Parameters	t 1 (mm)	t 2 (mm)	n (mm)	x (mm)	t (mm)
Category					
Experimental value	2	2	0.25	1.38	0.55
Simulation with segmented die	2	2	0.3	1.4	0.48
Simulation with integrate die	2	2	0.4	1.4	0.3

Fig.6 is the partial enlarged detail of metal flowing direction in two different dies. Metal flowing is assumed to slip between the adjacently laminar layers under the external force. With the sheets being compressed, the metal flows in the direction of least friction resistance. In other words, the metal flows into the interspace of the separate sections and both sides of punch if clinching with segmented die. When encountering the resistance again, the metal retraces and an eddy is produced. It can be seen that at time of 0.9s, clinching process with integrate die is completed. Because that the metal only flows to the sides of punch as a result of no interspace in the integrate die. While the clinching with segmented die is finished at 1.2s, which means the metal still flowing in the die cavity at 0.9s. This results in the metal flowing more sufficiently in integrate die cavity and a better interlocking obtained.

Summary

An energy saving joint method called clinch is analyzed by finite method. From the analysis of the numerical simulation, the conclusions can be drawn that simulating with segmented die will be more coincide with experimental test than integrate die. The reason why simulating with segmented die can get better neck thickness and undercut is that metal flows more sufficiently in segmented die cavity. The currently available work in this paper can be very helpful for engineers in order to design and optimize various metal forming process and tools.

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Design of Test Device for Carbon Dioxide Absorbents as Energy Materials Based on Pressure Sensor and Temperature Sensor

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Keywords: Sensors, Carbon dioxide absorbent, Test device

Abstract. This thesis introduces design principle, methods and composition of a new test device for carbon dioxide absorbents as energy materials based on pressure sensor and temperature sensor. The error of the test device is analyzed. The results show that the error of the device is acceptable after correcting, the error can be ignored. The test results are reliable.

Carbon dioxide absorbent is a necessary chemical materials used by closed and semi-enclosed diving apparatus. Its performance and quality directly related to the safety of diver. So the absorbent should be examined and tested before diving. The structure of the existing test device for carbon dioxide absorbents is more complex, operation is more difficult, and efficiency is lower. This paper introduces a new test device for carbon dioxide absorbents as energy materials based on pressure sensor and temperature sensor. Its accuracy is higher, and easy to operation. So it can be applied to basic unit.

1 Basic principle, components and technical parameters

The basic function of this test device is measurement for absorb capacity of carbon dioxide absorbent, and content of carbon dioxide and water.

1.1 Basic principle

According to the chemical characteristics of carbon dioxide absorbent, and the principle that hydrochloric acid and carbonate can produce chemical reaction and release carbon dioxide, the carbon dioxide volume content in each unit quality absorbent can be measured and calculated with pressure sensor and temperature sensor.

The relation in gas volume, temperature and pressure is ^[1]:

$$V_{\text{gas}} = f(P, T) \text{ (ml)} \quad (1)$$

Among them: V_{gas} —volume of gas, ml

P —pressure after reaction, ATA

T —absolute temperature after reaction, K

1.2 Composition and function

The test device for carbon dioxide absorbents mainly consists of the gas volume meter, absorb capacity tester, moisture measuring instrument, as shown in figure 1.

The gas meter is core part of the test device for carbon dioxide absorbents. It consists of reactor, gas transmission device, pressure and temperature measuring and displaying device, and computer detection system etc. It is mainly used for controlling chemical reaction of the absorbent, test and analysis of the carbon dioxide quantity in the absorbent by testing software, display and output the tested result.

The absorb capacity tester of carbon dioxide consists of pressure gas cylinders of carbon dioxide, decompression device, regulator flow meter, reaction tube, carbon dioxide absorption canister and rubber hose, etc. It is mainly used for making completely chemical reaction between absorbent and carbon dioxide. The tester is used together with the gas meter to measure carbon dioxide absorb capacity of the absorbent.

The moisture measuring instrument is an independent measuring instrument. It consists of precision balance, high temperature drying oven and weighing bottle. It is mainly used for measuring moisture content in carbon dioxide absorbent.

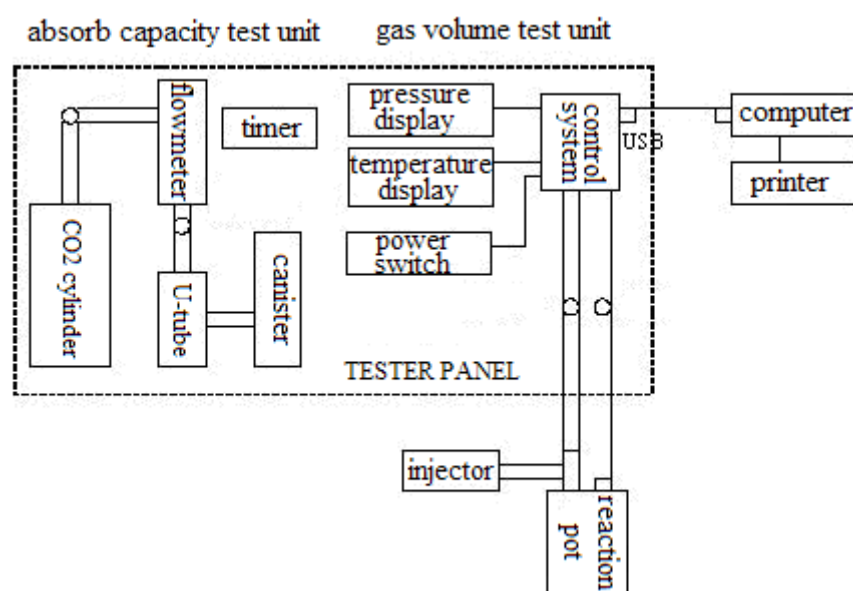


Fig.1 Composing of the test device

1.3 Mainly technical parameters

(1) The measurement range and requirements of absorbent

Absorb capacity: measurement range 45~240ml/g, error < $\pm 3\%$

CO₂: measurement range 7~40ml/g, error < $\pm 3\%$

Moisture: measurement range 5~40%, error < $\pm 1\%$

(2) The other requirements

Safety, reliability, simple to operation and maintenance, convenient for transportation and storage.

2 Results and analysis

The carbon dioxide levels and absorb capacity of an absorbent sample (090709) had been tested with the test device. The results and consistency see table 1.

Tab.1 Testing data and consistency

Test items	Contrast value (ml/g)	consistency (%)	measuring value (ml/g)	consistency (%)	normalized value (ml/g)	Qualified value (ml/g)
absorptivity	158.62	98.18	152.95	99.19	≥ 152.75	≥ 150
CO ₂ content	15.94	99.86	14.88	98.98	≥ 12.73	≥ 15

2.1 Results

The measurement result of carbon dioxide content in absorbent is higher of 16.89% than standard. The result is reasonable, and the consistency of the value is better. The measurement result of absorb capacity is higher of 0.13% than standard. The result is reasonable, and the consistency of the value is better.

The reason of measurement results of carbon dioxide content on the high side is the absorbent contacts with air and absorbs a little carbon dioxide in air in the course of carriage, storage and testing. Has nothing to do with the test device for carbon dioxide absorbents.

The errors between measurement results of absorb capacity and the standard is only 0.13%, and the consistency of the measured value is better also.

2.2 Error analysis

The factors of errors include the error of pressure sensor, the error of temperature sensor, the error of leak, the error of data communication and transmission, and the error of calculation model^[2].

(1) The error of pressure sensor

Pressure sensor measuring range is 0~35 kPa, and precision is 0.5 magnitudes. The sensor has the function of temperature compensation, and it can automatic correction zero offset error and sensitivity offset error. The maximum error of precision under 20 kPa pressure is ± 0.1 kPa, and this will led to measurement error is less than $\pm 0.60\%$.

(2) The error of temperature sensor

Temperature sensor measuring precision is $\pm 0.1^\circ\text{C}$. There is a piece of copper between temperature sensor probe and the testing medium, so the measured value is lower than actual temperature and time is delay (see figure2). The maximum error of temperature under 20 kPa pressure is 2.7°C , and this will led to measurement error is less than $+0.80\%$.

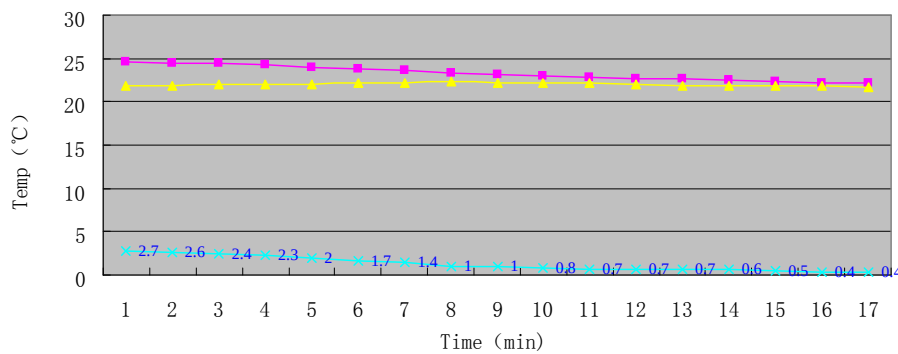


Fig.2 Measuring temperature, actual temperature and error curve

■ actual temperature ▲ measuring temperature × error

According to the contrast test results between the actual temperature and measuring temperature with sensor, method to reduce the error can be used by correcting the temperature with measuring with temperature sensors. After correcting the maximum error of temperature under 20 kPa pressure is $\pm 0.3^\circ\text{C}$ (see figure 3), and this will led to measurement error is less than $\pm 0.10\%$.

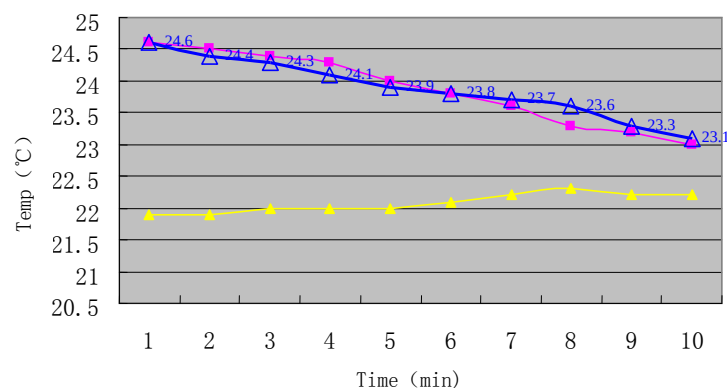


Fig.3 Contrast figure of measuring temperature, actual temperature and corrected temperature

■ actual temperature ▲ measuring temperature △ corrected temperature

(3) The error of leak

According to the result of actual test, the maxim leakage of big reaction tank under 30 kPa pressure is 0.16 kPa/min, the maxim leakage of small reaction tank is 0.12 kPa/min. The measuring error lead by leakage is shown in figure 4 shows. There is a linear relationship between leakage error and time, it can be corrected in accordance with the linear relationship.

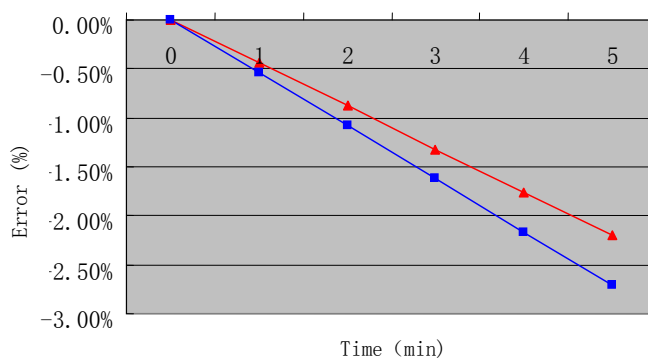


Fig.4 Error of leak

■ big reaction tank ▲ small reaction tank

(4) The error of system net volume

The measuring error of CO₂ is very large, because of the error of system net volume. Error is less than $\pm 7.2\%$ when the range of gas output is 100~160ml, and Error is less than $\pm 8.1\%$ when range is 10~20ml.

In order to calibrate reaction tank net volume value, the gas is quantitative pour into the system in the assembly stage. The measuring error of CO₂ after calibration: Error is less than $\pm 0.4\%$ when the range of gas output is 100~160ml, and Error is less than $\pm 0.98\%$ when range is 10~20ml.

(5) Total error

Contrast before and after correction of system measurement error is shown in table 2. Through this error correction, total gas measurement error is not more than $\pm 1.65\%$.

Tab.2 Contrast of system error and error before and after correcting

Error types	Pressure sensor	Temperature sensor	Gas leakage	System net volume	Total error
Before correction, %					
big reaction tank	± 0.52	$+0.80$	-0.68^*	± 7.2	$-7.60/+7.84$
small reaction tank	± 0.57	$+0.80$	-0.74^*	± 8.1	$-8.61/+8.73$
Afer correction, %					
big reaction tank	± 0.52	± 0.10	0	± 0.40	± 1.02
small reaction tank	± 0.57	± 0.10	0	± 0.98	± 1.65

Note: * the maximum error of gas leak in unit time.

The quantitative gas calibration test found that the error of system net volume actually reflect comprehensive error of the test device for carbon dioxide absorbents. It includes the pressure sensor linear error, the temperature sensor error, and the error of data communication and transmission. All of the error can be corrected except system leakage error, through calibrating reaction tank net volume value. Based on the statistical analysis to the tested data, we have got the correction formula to the system net volume value.

After correcting to mathematical model with the formula, we do the calibration test of quantitative purring gas again, the test results shown in table 3. The results show that after the correction of mathematical model, the measuring error of the test device for carbon dioxide absorbents basically eliminated in theory^[3].

Tab.3 The test results of quantitative gas correcting and measurement error after model correcting

Item	Standard gas (ml)	Pressure (kPa)	Temprature (°C)	Measured value (ml)	Error (%)	The maximum error (%)
big reaction tank	100	12.193	17.82	100.00	0.002	$\neq 0.012$
	120	14.628	17.63	120.00	0.000	
	160	19.542	18.00	159.98	0.012	
small reaction tank	10	7.830	18.35	10.00	0.001	$\neq 0.010$
	15	11.638	18.40	15.00	0.001	
	20	15.378	18.44	20.00	0.010	

3 Conclusions

In this paper, follow design parameters are analyzed: Composition, function and precision of the test device for carbon dioxide absorbents.

The result shows that the error of the device is acceptable. And after correcting with mathematical model, the error can be eliminated basically. The test results are reliable.

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Study of improving cleanness on master alloy of Energy Material

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Keywords: inclusion; cleanness; alloy

Abstract: The largest proportion of element in master alloys were iron and pure iron smelting industrial used accounts for 70% of the total raw materials. Iron produced by secondary refining has the highest purity. If the inclusion in the raw materials is very low, inclusions in smelting amorphous master alloy would be lower. The carbon content of 0.1% in the carbon-75 ferrosilicon, but ferrosilicon dosage is small, generally is about 10%, so the carbon content in the master alloy is below 0.01%. Boron anhydride generally containing boron oxide at about 95%, the rest is mainly water, contains less impurities, the alumina content is generally below 0.1%, as well as chloride, which have little effect on master alloy smelting. Impurities in additive calcium oxide, calcium fluoride are generally below 10%, mainly are oxides, presenting in the slag in the smelting master alloys basically.

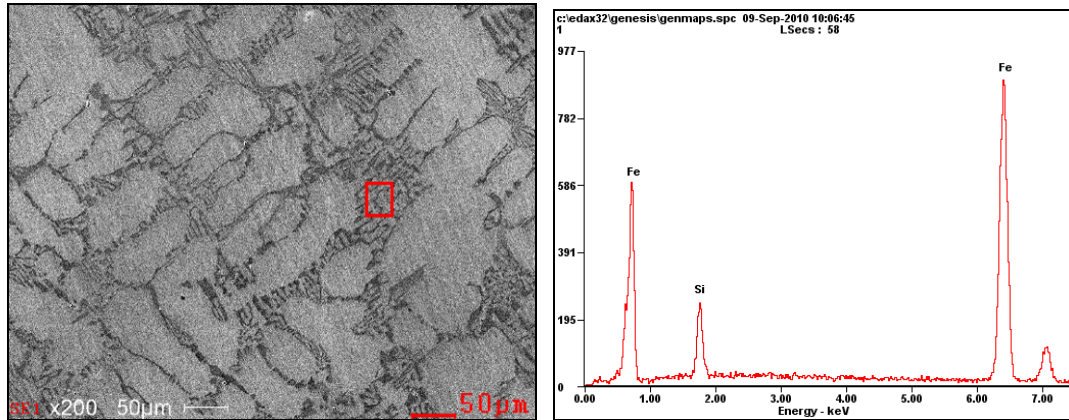
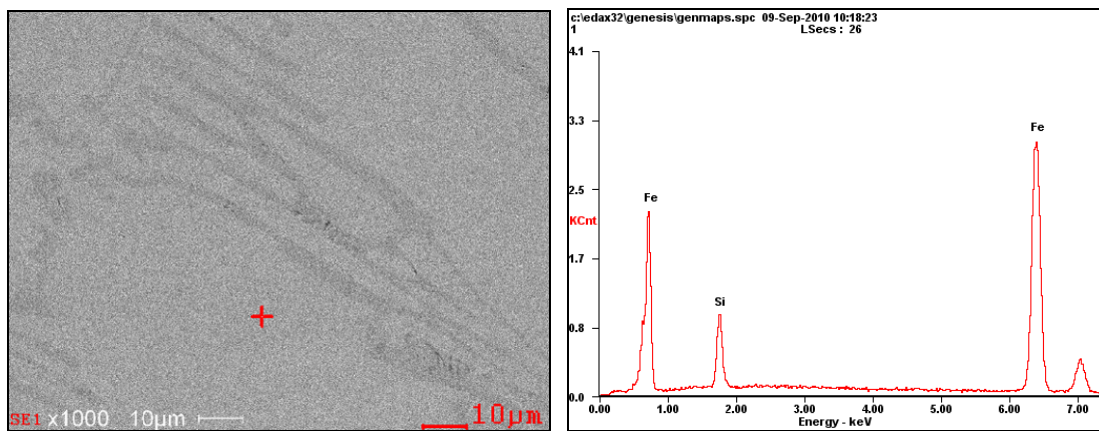
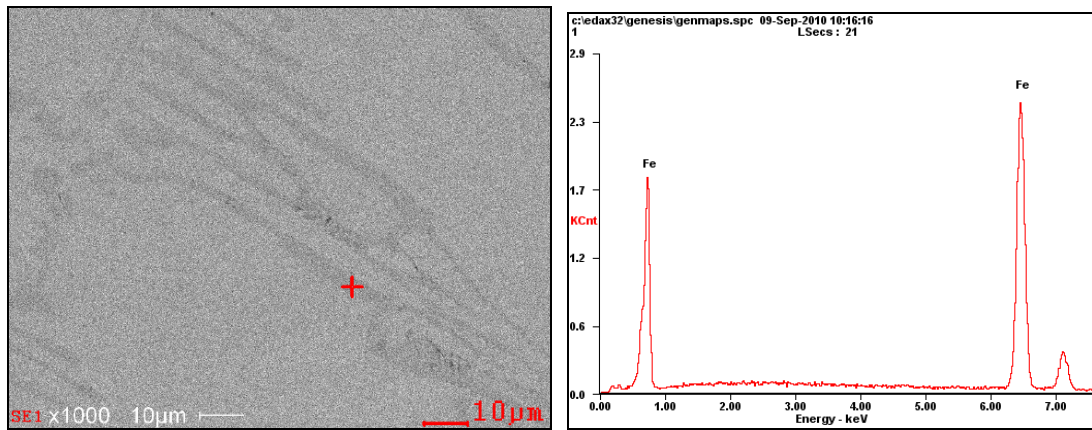
Introduction

A large number of slag were generated, when amorphous master alloy were smelted. Inclusion was absorbed by the slag, when float up to the interface of slag and iron. The more slag there is, the greater capacity of absorption and dissolution of inclusions is. But a very large amount of slag will increase the refractory erosion, affecting refractory's life, and we need to recycle slag to re-use it. It is very important to remove inclusions that calcium oxide content in the slag composition. Increasing alkalinity can enhance the slag capacity of absorption inclusions[1~2]. Smelting amorphous master alloy should have a reasonable amount of slag mainly by controlling the final slag alkalinity around 1.0. We can remove the inclusions produced by the amorphous master alloy solution effectively, improving the cleanliness of the master alloy.

1 The experimental samples

Samples were obtained from the smelting of the spindle. After preparation, grinding, polishing, they were observed by a JSM-600 scanning electron microscope. Ferrosilicon is an essential component of the agent and reducing agent in the smelting amorphous master alloy [3~5]. As for ferrosilicon smelting are generally produced by carbothermal reduction, so it inevitably contain a certain amount of carbon.

From Fig. 1 we can see, in the 200 times magnification field of view, there are some pale area and gray bar area, all are iron and silicon, without any other impurities. Irregular light gray bar in the 100 times magnification field of view pale area on the substrate can be seen from Fig. 2 and Fig. 3, the whitish district matrix are iron and silicon, and light gray bars is iron. The sample composition is very pure, iron, bit segregation is found in the local when solidification of iron, but it does not affect the cleanliness. The experimental results show that master alloy smelted by low-temperature direct reduction has higher cleanness.

Fig. 1 SEM image of sample ($\times 200$)Fig. 2 SEM image of sample ($\times 1000$)Fig. 3 SEM image of sample ($\times 1000$)

2 Analysis of chemical component

A spectral analysis on the samples, as shown in Table 1, in addition to iron, silicon and boron, other elements' content are tiny and the content of nitrogen is only 1ppm which is lower than the theoretical analysis indicating that raw material is suitable and atmosphere is well protected. The oxygen content that determined by chemical analysis is 0.0010% which is higher than the theoretical in master alloy, but to meet the requirements. The carbon content is 0.0093% and aluminum content is 0.0002%. They also met the requirements. That sample is difficult to form endogenous inclusions, even if there are exogenous inclusions, most of them have been absorbed by the slag in the smelting process.

Table 1 Chemical component of sample

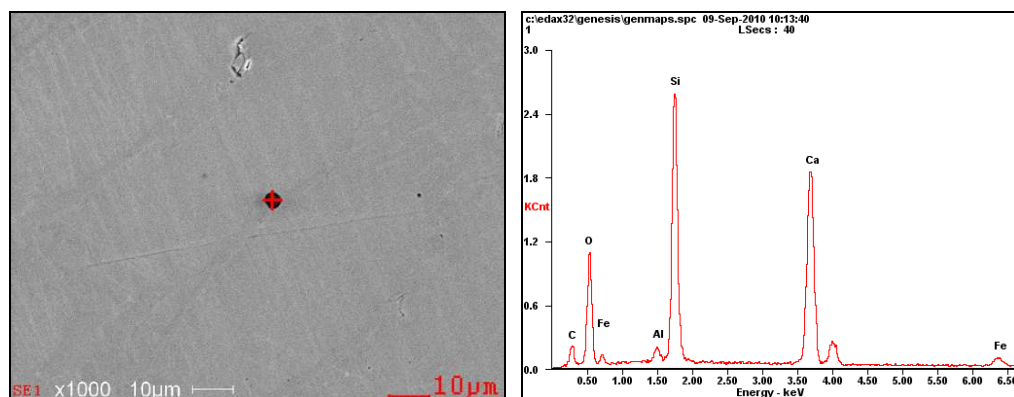
Si	B	Mn	C	P	S	Al	Cr	Cu	N
6.61	1.94	0.0289	0.0093	0.0071	0.0083	0.0002	0.0376	0.0756	<0.0001
Mo	Co	Nb	Ti	V	W	Pb	Ca	Sb	Fe
0.0057	0.0014	0.0005	0.0012	0.0006	0.0011	0.0006	<0.00003	<0.0004	91.2

3. The size of inclusion

Non-metallic inclusions will destroy continuity and compactness of master alloy matrix, which can do a great harm to processing performance and functional performance of strips later sprayed. Therefore we need to study the size and number of nonmetallic inclusions in the master alloy. According to the theory of metal fracture, when the inclusion size is less than $8\mu\text{m}$, under the action of the stress load, there is no crack source on the interface of the inclusions and metal, therefore people regard $8\mu\text{m}$ as the critical size of inclusions. Usually inclusion's size in clean steel should be below $8\mu\text{m}$.

Less inclusions are found in the sample. 30 field of view were arbitrarily selected on the sample surface which are used to observe, recording the size of the inclusions. The number of the inclusion with size of $1\mu\text{m} < d < 4\mu\text{m}$ is 14, accounting for 37% of the total; the number of $4\mu\text{m} < d < 8\mu\text{m}$ is 21 accounted for 55% of the total and the number of $d > 8\mu\text{m}$ is 3, which accounted 8% of the total. The figure shows, inclusion's size in the sample is mainly below $8\mu\text{m}$, mainly concentrated in about $4\mu\text{m}$, with smaller size, inclusions of larger than $8\mu\text{m}$ rarely can be seen, indicating that exogenous inclusions are also rare, most of which have been absorbed by the slag when floating.

Observing the sample by the scanning electron microscope, as shown in Fig. 4, the number of whose size less than $4\mu\text{m}$ of the inclusions is very small in the 1000 times magnification field of view. The big black spherical inclusion whose size was only $4\mu\text{m}$, mainly are silicate oxide inclusions containing trace amounts of aluminum and carbon. Transform the scan field of view and magnification, but the nitride has not been found. Sulfide can be found in the tested sample, but its number is very small. Representative sample is shown in Fig. 5, the dimensions are less than $4\mu\text{m}$. They are mainly titanium and manganese inclusions. The chemical compositions of inclusion are shown in Table 2.

Fig. 4 Include A in sample ($\times 1000$)

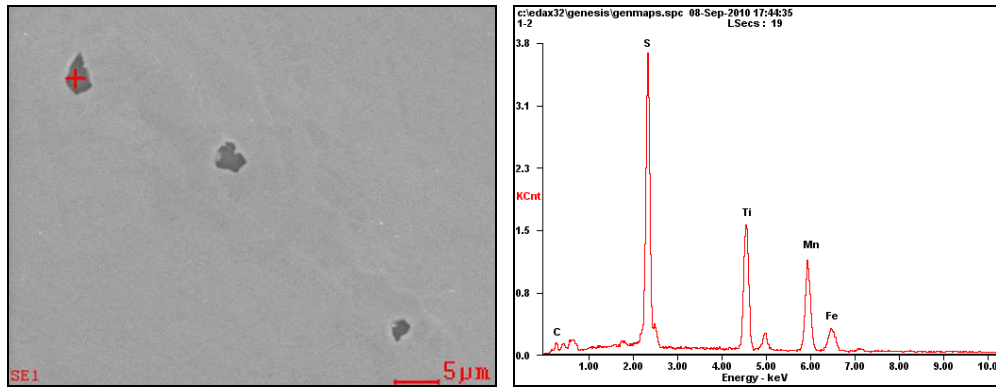
Fig. 5 Include B in sample ($\times 1000$)

Table 2 Main chemical component of inclusion

Sample	Element	Al	C	O	Si	Ca	S	Ti	Mn	Fe
A	wt%	1.35	11.87	43.50	20.10	20.49	-	-	-	2.70
	at%	0.99	19.63	54.04	14.22	10.16	-	-	-	0.96
B	wt%	-	11.47	-	-	-	28.41	24.37	29.13	6.62
	at%	-	31.86	-	-	-	29.55	16.96	17.68	3.95

4 Conclusions

By analyzing its mechanism and the process, we can take effective measures to reduce the inclusion content in the master alloy.

(1) The raw material is the main source of the master alloy harmful elements. To control impurities of oxygen, nitrogen, carbon and other elements of the various raw materials into the furnace are very important.

(2) The induction furnace take the flowing argon gas as the protective atmosphere, and keep the slight positive pressure operation from the beginning to the end to prevent the gas entry. Moreover, the slag covers the upper of the master alloy.

(3) We can use the interaction of bubble and master alloy solution to remove some inclusions and gas in the master alloy solution.

Acknowledgements

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Study on CO₂ Emission Constraint based on New Energy Materials for Generation Permits Trade

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Keywords: generation permits trade, economic generation dispatch, profit allocation, new energy materials

Abstract: Generation permits trade plays a key role in the economic generation dispatch. The application of new energy materials has a positive influence on the generation fuel mix, which offers cleaner power option for generation permits trade. An optimization model on generation permits trade is established to promote the development of renewable energy and the lowest generation cost of a certain unit commitment. Power demand, ramp-up limit, real power of a unit, new energy materials, and a certain emission limit are applied as the constraints of the model. The process of generation permits trade is a cooperative game. An optimized profit allocation model is also established using Shapley value to effectively allocate the profits among the units participating in the generation permits trade.

1. Introduction

China is now the world's second largest energy consumer, only after the USA. Along with the rapid economic development and ever increasing energy demand, not only the energy supply is tensioned, but also a lot environmental issues occur. As one of the major polluters in China, power plants contribute to half of the nation's SO₂ and CO₂ emissions and 20% of the industrial solid waste. To address these environmental issues, China has issued a series of polices, regulations and standards aiming to curb the pollution and improve the energy efficiency in the power sector. For example, as early as in 1991, Emission Standards of Air Pollutants for Thermal Power Plants (GB 13223-1991) was published, setting the emissions ceiling of smoke dust, SO₂, NO_x. This standard was amended three times afterwards till 2011 (in 1996, 2003 and 2011 respectively). The 2011 version (GB13223-2011) which is implemented from 1st, Jan. 2012 involves a highly constrained limitations for the emission of SO₂ (200 mg/m³ for existing power plants, 100 mg/m³ for new plants) and NO_x (100 mg/m³ for both existing and new power plants). In 2003, the central government issued Regulation on Pollution Charges Management, specifying the pollution charges for various pollutants.

Nowadays, addressing climate change caused by excessive GHG emissions is on the top agenda of the Chinese government. A commitment that China will decrease the carbon intensity per unit GDP by 40-45% by 2020 was made at the UNFCCC international climate change conference (COP 15) in 2009 in Copenhagen. As the nation's main emitter, power sector also plays a key role in achieving the above goal. Energy-saving generation dispatch is a crucial pathway for the thermal power plants to reduce the emissions. To date, Henan, Guizhou, Sichuan have been carrying out such demonstrations. There are a lot of researches on energy-saving generation dispatch, most of which focus on the different options of the unit commitment and the optimization of the dispatch effectiveness. In addition, new energy materials are also a key part of addressing climate change. This paper will introduce the pollution charges as part of the generation cost into the current economic generation dispatch model, establishing the optimization model on generation permits exchange. We also use the Shapley model to optimize the profit allocation between the parties participating in the exchange.

2. Optimization model for generation permits trade with a certain CO₂ emission constraint

2.1 Objective function

The objective of the economic generation dispatch is to achieve the lowest generation cost at the whole power supply system level with the existing generation capacity and fuel resources. To optimize the conventional economic generation dispatch model, a series of constraints should be introduced.

Assuming the number of units participating in the economic dispatch in a certain time period is n . This time period is further divided into t smaller time intervals. Then the objective function can be presented as follow,

$$(P1) \quad \min \sum_{t=1}^T \Delta T_t \sum_{i=1}^n u_{it} (a_i g_{it} + b_i g_{it}^2) (p_{coal} + p_{co2} * \kappa_{co2})$$

where, ΔT_t denotes the duration of the time interval, and for convenience, we assume that $\Delta T_t = 1$;

the binary variable u_{it} represents the status of unit i during period t , $u_{it} = 1$ if the unit i is on operation during period t , $u_{it} = 0$ otherwise; $a_i g_{it} + b_i g_{it}^2$ represents the coal consumption of unit i during period t ; g_{it} represents the available output of unit i during period t ; p_{coal} represents the unit price of the standard coal; κ_{co2} represents the CO₂ emission per unit standard coal; p_{co2} represents the price of CO₂, in terms of pollution charge or carbon tax.

2.2 Model constraints

The objective function above is subject to the following constraints.

2.2.1 power demand

The total of power generation of all the units during period t should not exceed the demand D_t .

$$\sum_{i=1}^n u_{it} g_{it} = D_t \quad (1)$$

2.2.2 ramp-up limit

Since the ramp up of the unit takes time, the ramp-up limit should be included.

$$|g_{it} - g_{i,t-1}| \leq \Delta g_i \quad (2)$$

2.2.3 The real power constraints

The real power of unit i has both upper limit and lower limit, so the real power of unit i should be constrained.

$$u_{it} g_{i \min} \leq g_{it} \leq u_{it} g_{i \max} \quad (3)$$

2.2.4 emission limit

To curb the emission of power generation, a certain emission ceiling should be given to a unit. The amount of pollutant emit by each unit should be lower than this limit. In this paper, we consider the pollutant as CO₂, so the following constraint is necessary.

$$\sum_{t=1}^T \Delta T_t \kappa_{co2} u_{it} (a_i g_{it} + b_i g_{it}^2) \leq \infty_{2i \max} \quad (4)$$

where, $\infty_{2i \max}$ represents the maximum of CO₂ emission from unit i during period t .

2.2.5 contract performance constraint

In a process of generation permits exchange, each party has the obligation to execute the contract. Therefore, the amount of power generated by unit i during the whole period T should not be less than the contractual amount.

$$\sum_{t=1}^T u_{it} g_{it} \Delta T_t \geq Q_{ci} \quad i=1,2,\dots,n ; \quad t=1,2,\dots,T \quad (5)$$

where Q_{ci} represents the contractual amount of power generation of unit i .

2.2.6 runtime and downtime constraints

$$(T_{i,t-1}^{on} - MT_i^{on})(u_{i,t-1} - u_{it}) \geq 0 \quad (6)$$

$$(T_{i,t-1}^{off} - MT_i^{off})(u_{it} - u_{i,t-1}) \geq 0 \quad (7)$$

where $T_{i,t-1}^{on}$ represents the runtime of unit i during period $t-1$; MT_i^{on} represents the lower limit of runtime of unit i ; $T_{i,t-1}^{off}$ represents the downtime of unit i during period $t-1$; MT_i^{off} represents the lower limit of downtime of unit i . Therefore, Eq. (6) is the constraint of the runtime of unit i , and Eq. (7) is the constraint of the downtime of unit i .

3. Optimization model for profit allocation of generation permits trade based on Shapley value

3.1 Shapley value

Cooperative game means through cooperation, both parties can gain more profit, or at least one party gains more profit without damaging the other one's interest. In other words, the profit of the coalition will be higher than each individual party can get without cooperation. Cooperative game theory can be used to study the profit allocation issue, as a surplus can always be gained after the cooperative game. Shapley Model is a typical cooperative game model.

Denote a group of players as a set N , where $N = \{1, 2, \dots, n\}$. $V(S)$ is the corresponding function value of an arbitral sub-set S . $V(S)$ represents the profit gained by a player through cooperation. $V(S)$ satisfies the following constraints.

$$V(\emptyset) = 0 \quad (8)$$

$$V(S_1 \cup S_2) + V(S_1 \cap S_2) \geq V(S_1) + V(S_2) \quad (9)$$

If we consider each player is independent, Eq. (9) can be described as Eq. (10),

$$V(S_1 \cup S_2) \geq V(S_1) + V(S_2) \quad (10)$$

Denote $[N, V]$ as the cooperative solution, so V represents the characteristic function of the solution.

If we denote X_i as the profit player i gain from the maximum collective profit $V(N)$, $X = (X_1, X_2, \dots, X_n)$ represents the allocation solution of the cooperative game.

Shapley value should satisfy the following three axioms.

- Efficiency. If player i does not contribute to the coalition, no profit will be allocated to him. All the individual profits add up to the total profit. This can be described mathematically as the Eq.(11).

$$\text{If } V(S-i) = V(S), X_i(V) = 0$$

$$\sum_{i=1}^n X_i = V(N) \quad (11)$$

- Dummy player. In a coalition, the profit a player will be allocated only relate to its contribution to the coalition, nothing to do with his order or mark.

Assuming π is a permutation of set N , $N=\{1,2, \dots, n\}$, π_i is the mapping of i , π_s is the mapping of S , $S \subset N$. If we denote $V(\pi_s)=U(S)$, we can have the following equation,

$$X_{\pi_i}(V) = X_i(U) \quad i=1,2, \dots, n \quad (12)$$

- c. Additivity. If two coalitions are proceeding simultaneously by the same group of players, the total profit should be the sum of the profit each player gain from both coalitions. This can be described mathematically as followings.

$$X_i(U+V) = X_i(U) + X_i(V) \quad i=1, 2, \dots, n \quad (13)$$

where, U and V are two arbitrary characteristic functions of set N .

From the above, the allocation solution of cooperative game X_i can be described as follows.

$$X_i(V) = \sum_{S \subset N} W(|S|) [V(S) - V(S-i)] \quad (14)$$

$$W(|S|) = \frac{(n-|S|)! (|S|-1)!}{n!} \quad (15)$$

where, S represents all the subsets the player i belongs to; $|S|$ represents the number of players in subset S ; $W(|S|)$ represents the weighted factor; $V(S)$ represents the profit of coalition S which player i belongs to; $V(S-i)$ represents the profit of the coalition which player i does not belong to. $N=\{1,2, \dots, n\}$, $i=1,2, \dots, n$.

3.2 Optimization model on profit allocation of generation permits trade with CO2 emission constraint

Denote I as the set of all the solutions of unit commitment (the coalitions), $I=\{I_1, I_2, \dots, I_m\}$. We can describe the coalitions mathematically as follow,

$$\sum_{i \in I_j} \sum_{t=1}^T u_{it} g_{it} \geq \sum_{i \in I_j} u_{it} Q_{ci} \quad (16)$$

$$\sum_{i \in I_j} \sum_{t=1}^T \kappa_{co2} u_{it} (a_i g_{it} + b_i g_{it}^2) \leq \sum_{i \in I_j} u_{it} \omega_{2i \max} \quad (17)$$

Then the objective function can be expressed as Eq. (18)

$$(P2) \quad F^*(i|i \in I_j) = \min \sum_{t=1}^T \sum_{i \in I_j} u_{it} (a_i g_{it} + b_i g_{it}^2) (p_{coal} + p_{co2} * \kappa_{co2}) \quad (18)$$

The total profit of coalition I_j can be calculated as Eq.(19).

$$V^*(i|i \in I_j) = \sum_{t=1}^T \sum_{i \in I_j} u_{it}^* g_{it}^* p_{it} - F^*(i|i \in I_j) \quad (19)$$

where, p_{it} represents the on-grid price of unit i during period t .

Then, the total profit of all the coalitions I can be calculated as Eq. (20).

$$V^*(i|i \in I_m) = \sum_{t=1}^T \sum_{i \in I_m} u_{it}^* g_{it}^* p_{it} - F^*(i|i \in I_m) \quad I_m=\{1,2, \dots, n\} \quad (20)$$

Then, the profit unit i gets from the coalitions can be calculated as Eq. (21).

$$X_i^*(V) = \sum_{S \subset N} W(|S|) [V^*(i|i \in I_j) - V^*(k|k \in I_j - i)] \quad (21)$$

Finally, the coal consumption and CO₂ emission of unit i can be calculated as follows.

$$Coal^* = \sum_{t=1}^T \sum_{i=1}^n u_{it} (a_i \overline{g_{it}} + b_i \overline{g_{it}}^2) \quad (22)$$

$$CO_2^* = \sum_{t=1}^T \sum_{i=1}^n u_{it} (a_i \overline{g_{it}} + b_i \overline{g_{it}}^2) \kappa_{co2} \quad (23)$$

4. Conclusion

The development of new energy materials provides cleaner power options for generation permits trade. The large scale spread of nuclear energy, solar energy, wind energy and biomass energy all depends on the advanced energy materials. It also plays a determinative role in the energy storage field, which would thoroughly change the mode of energy supply, and dramatically promote the development of renewable energy.

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Magnetic properties and glass forming ability of Fe-B-Y-Nb-Zr bulk metallic glasses

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Abstract. Bulk metallic glasses (BMGs) alloys (Fe_{71.2}B₂₄Y_{4.8})₉₆Nb_{4-x}Zr_x (x = 1-4 at.%) with a maximum diameter of 5 mm were synthesized with low purity materials by copper mold casting technique. The effect of Zr substitution for Nb on the structure, thermal stability and the magnetic properties has been studied. It was found that the substitution of an appropriate amount of Zr for Nb can improve the glass forming ability. The wide supercooled liquid region ΔT_x (exceeding 123 K) and a high T_g (exceeding 868 K) demonstrated a high thermal stability of the present Fe-based BMGs. In addition, these BMGs also exhibit good soft magnetic properties with relatively high saturation magnetization of 88 emu/g, and low coercivity of 20 Oe.

1. Introduction

Since the first synthesis of Fe-based ferromagnetic bulk metallic glasses (BMGs) in 1995 [1], a large number of Fe-based BMGs have been developed for their excellent soft magnetic properties and potential magnetic applications [2,3]. However, most of the Fe-based BMGs were prepared using high purity raw materials, because a trace amount of oxygen or other impurities would induce heterogeneous nucleation and reduce glass-forming ability (GFA) drastically. Fluxing using B₂O₃ can effectively remove oxygen or impurities from the raw materials used, thus can improve the glass forming ability of Fe-based BMGs systems [4]. However, this method is quite complicated and time-consuming, and not appropriate for scale-up production. There has been strong demand for the development of Fe-based bulk metallic glasses with high GFA and using low purity materials from the viewpoint of industrial applications.

In order to enhance the glass forming ability and improve the magnetic properties of metallic glasses, extensive efforts have been made in recent years by compositional and structural design [5,6]. Some results [7] show that the addition of "alike" chemical elements can obviously improve the magnetic properties and the glass-forming ability of amorphous alloys, thus this strategy was used to synthesize a series of new type of bulk ferromagnetic glassy alloys. The "alike" means that the elements have similar atomic size, physical and chemical properties. However, the detailed mechanism for the improvement of GFA and magnetic properties has not been fully understood. In this paper, we have developed a new Fe-based system with the composition of (Fe_{71.2}B₂₄Y_{4.8})₉₆Nb_{4-x}Zr_x (x = 1-4 at.%). The emphasis of the present study focused on the effect of Zr substitution for Nb (Zr and Nb are the alike elements) on the glass forming ability and magnetic properties by using low purity materials.

2. Experimental

Multi-component master alloys with compositions of (Fe_{71.2}B₂₄Y_{4.8})₉₆Nb_{4-x}Zr_x (x = 1, 2, 3 and 4 at.%) were prepared by 6-7 times arc melting of raw materials under a titanium metal gettered argon atmosphere. The raw materials include industrial pure Fe (99.5 wt.%), Zr (99.8 wt.%), Y (99.5 wt.%), Nb (99.5 wt.%) and industrial Fe-B alloy which consists of 81.1 wt.% of

Fe, 17.9 wt.% of B and other impurities of Al, Si, C, S, P and their oxides in remainder. Sample rods with a diameter of 2-5mm and a length of 50mm were produced by suck casting method. The structure of the as-cast alloys was identified by X-ray diffraction (XRD, Philips X'Pert PRO) using Cu -K α radiation. The thermal properties associated with glass transition, crystallization and melting events of amorphous alloys were characterized by differential thermal analyzer (PerkinElmer, DTA-7) using Al₂O₃ pan under argon atmosphere at heating rate of 20 K/min. DTA system was calibrated for temperature by using Al and Ag standards, giving an accuracy of ± 0.2 K. Magnetic measurements were carried out with a vibrating sample magnetometer (VSM, Lake Shore-7410) under an applied magnetic field of 4 kOe at room temperature.

3. Results and discussion

Figure 1 shows the XRD patterns of the as-cast (Fe_{71.2}B₂₄Y_{4.8})₉₆Nb₄ samples with size of 3–5 mm diameters. It can be observed that the alloy with rod size of 4mm or less is almost fully amorphous as no any Bragg peaks can be detected in the XRD patterns. However, when the rod increases up to 5 mm, a few of Bragg peaks appear in its XRD pattern, demonstrating that the critical size for glass formation for (Fe_{71.2}B₂₄Y_{4.8})₉₆Nb₄ alloy is roughly 4 mm. Fig. 2 shows the XRD patterns of the (Fe_{71.2}B₂₄Y_{4.8})₉₆Nb_{4-x}Zr_x alloy with the substitution of different amount of Zr for Nb. The alloy (Fe_{71.2}B₂₄Y_{4.8})₉₆Nb₃Zr₁ with 5 mm diameter can be cast into fully amorphous as no Bragg peaks except for a broad diffraction hump appeared in the XRD pattern. Compared to the (Fe_{71.2}B₂₄Y_{4.8})₉₆Nb₄ alloy, the substitution of an appropriate amount of Zr for Nb (1 at%) could slightly enhance the glass forming ability (GFA) of the Fe-based system. However, further increasing Zr content could deteriorate the GFA of the system, for instance, a fully glass rod of 4 mm can be cast for 2 at% Zr. The critical size for glass formation could be rapidly reduced down to less than 2 mm if Zr substitution exceed 3at %

Fig. 3(a) shows the DTA curves of as-cast (Fe_{71.2}B₂₄Y_{4.8})₉₆Nb_{4-x}Zr_x (x = 0, 1, 2, 3 and 4 at.%) alloys of 2mm diameter with different Zr contents at temperatures up to 1200 K. It can be seen that, each alloy exhibits a distinct glass transition followed by a wide supercooled liquid region before crystallization and all alloys follow a multi-stage of crystallization process except the alloy of x=4, which does not shows any thermal relation in this temperature range, indicating that this alloy, in consistent with XRD results, is fully crystallized. Based on the DTA curves, glass transition temperature (T_g), the onset crystallization temperature (T_x) and supercooled liquid region ($\Delta T_x = T_x - T_g$) are derived and summarized in Table 1. It can be seen that the ΔT_x and T_g of all alloys except x=0 and x=4 are exceeding 115 K and 835 K, respectively, indicative of a high thermal stability of the present Fe-based BMG. Especially, the alloy with 1at% Zr exhibits ΔT_x and T_g are 123K and 877 K, respectively, which are the highest among the alloys studied. Fig. 3(b) shows the DTA curves at

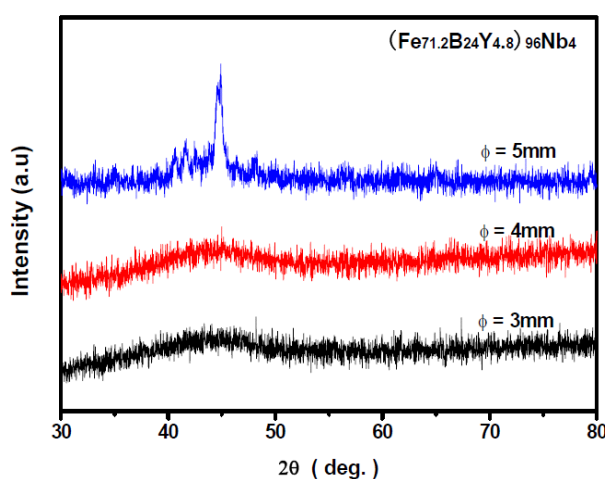


Fig.1 The XRD patterns of the (Fe_{71.2}B₂₄Y_{4.8})₉₆Nb₄ glassy alloys with diameters 3–5 mm

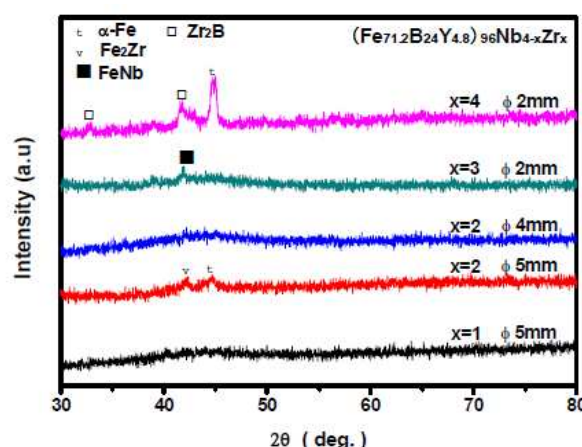


Fig.2 The XRD patterns of the (Fe_{71.2}B₂₄Y_{4.8})₉₆Nb_{4-x}Zr_x (x=1, 2, 3 and 4) glassy alloys with diameters 2–5 mm

high temperature range (i.e., 1200~ 1450 K), which illustrate the melting reaction of different Fe-based alloys. The melting temperature T_m and liquid temperature T_l are also included in Table 1. All the alloys exhibit one melting peak, indicating that the alloys are close to the eutectic composition, even with different amount of Zr. The reduced glass transition temperature $T_r (=T_g T_g / T_l)$ and parameter $\gamma (=T_x / T_g + T_l)$, which are usually taken as the gauges for glass forming ability, are calculated and also presented in Table 1. It is found that the alloy (Fe_{71.2}B₂₄Y_{4.8})₉₆Nb₃Zr₁ has the highest T_{rg} of 0.623 and largest γ of 0.438, demonstrating a best glass forming ability. This is in a good agreement with the largest critical size for glass formation in this alloy.

To investigate the effect of Zr substitution on magnetic properties of the Fe-based BMGs, the hysteresis M-H loops of all as-cast alloys were measured with VSM under the applied magnetic field of 4 KOe. Fig. 4 shows the M-H loops of the alloys with rod diameter of 2 mm. The shape of M-H loops for all alloys shows a typical ferromagnetic feature, i.e., magnetization rises sharply with increasing applied field at the lower field side and approaches gradually the saturation under the higher field. The saturated magnetization (M_s) and the coercivity (H_c) of the alloys derived from each of M-H curves are also listed in table 1. It is found that the M_s increases initially with Zr content up to 3 at.%, then decreases. The alloys with $x = 3$, which are actually composites containing partial crystalline phases in amorphous matrix, have obviously higher M_s . However, the H_c keeps almost unchanged in the alloys of $x=0-3$. The highest saturation magnetization of 88 emu/g and the lowest coercivity of 20 Oe was obtained in the alloy with 2 at% Zr. This demonstrates that a proper Zr substitution can also improve the soft magnetic properties of the Fe-based BMG.

The results demonstrate that a proper Zr substitution for Nb can enhance the glass forming ability of (Fe_{71.2}B₂₄Y_{4.8})₉₆Nb₄ alloy as indicated by the formation of 5 mm fully amorphous rods even using industrial raw materials. This is probably due to the fact that the substitution increases the satisfaction of the empirical rules proposed by Inoue [8]. First, the Zr addition makes the FeBYNb system more complicated, Secondly, the addition of a suitable amount of Zr (around 1–3 at.% in the present study) would lead to a more sequential change in the atomic size in the order of Y>Zr>Nb>Fe>B, which may enhance the viscosity of alloy. Furthermore, the enthalpies of mixing are -25 kJ/mol for the Zr-Fe pair, -56 kJ/mol for the Zr-B pair, which are larger than those for Nb-Fe and the Nb-B pairs respectively [9]. The above factors together would result in a denser topological package of atoms and hinder one another from crystallization, as a result, enhance the stability of under-cooled alloy melt and increase the glass forming ability.

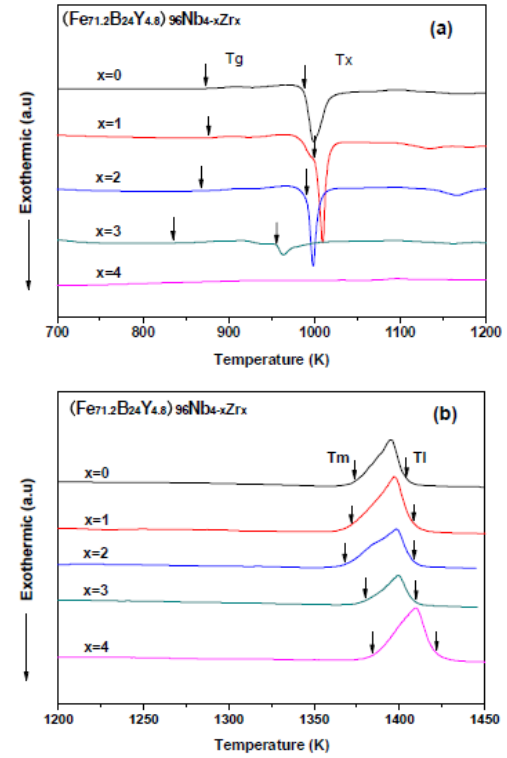


Fig.3 The DTA curves of the casting (Fe_{71.2}B₂₄Y_{4.8})₉₆Nb_{4-x}Zr_x ($x=0, 1, 2, 3$ and 4) metal alloy with diameter of 2 mm

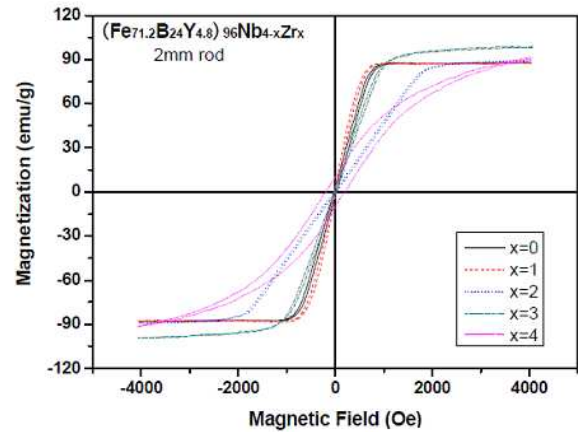


Fig.4 The M-H loops of as-cast (Fe_{71.2}B₂₄Y_{4.8})₉₆Nb_{4-x}Zr_x ($x=0, 1, 2, 3$ and 4) glassy alloys with diameters 2 mm at room temperature

The substitution of a proper amount of Zr for Nb can also slightly improve the soft magnetic properties of Fe-based BMG, as demonstrated by the increase in saturated magnetization without change of coercivity (see table 1). The maximum M_s of 99 emu/g was obtained in the alloy with $x=3$, which is actually a composite containing amorphous phase and a small amount of FeNb inter-metallic. Since the crystalline phases of FeNb are of strong ferromagnetism, which has a coupling interaction with amorphous phase, leading to the significant increase in M_s . However, as the Zr content increases up to 4 at.%, the alloy is fully crystallized, the coupling interaction disappears, thus causing the reduction of M_s as shown in Fig. 4 and table 1.

Table 1 Thermal parameters of as cast $(\text{Fe}_{71.2}\text{B}_{24}\text{Y}_{4.8})_{96}\text{Nb}_{4-x}\text{Zr}_x$ ($x = 1, 2, 3$ and 4 at.%) alloy rods with diameters of 2mm

Alloys	$T_g(\text{K})$	$T_x(\text{K})$	$\Delta T_x(\text{K})$	$T_m(\text{K})$	$T_l(\text{K})$	$\Delta T_m(\text{K})$	T_{rg}	γ	$M_s(\text{emu/g})$	$H_c(\text{Oe})$
X=0	873	988	115	1373	1404	31	0.622	0.434	88	0.5
X=1	877	1000	123	1372	1408	36	0.623	0.438	89	0.5
X=2	868	991	123	1368	1409	41	0.616	0.435	90	0.7
X=3	835	956	121	1380	1409	29	0.593	0.426	99	3.8
X=4	/	/	/	1384	1422	38	/	/	92	24.5

4. Conclusions

New Fe-based bulk metallic glasses containing Zr with a maximum 5mm in diameter are successfully developed using low purity materials by copper mould casting method. The effect of Zr substitution for Nb on the magnetic properties and glass forming ability has been investigated. The substitution of an appropriate amount of Zr (i.e., 1 at.%) can enhance the GFA because of increasing the satisfaction of Inoue's empirical rules. The Fe-based BMGs exhibit a large supercooled liquid region (exceeding 123 K) and high glass transition temperature (exceeding 868 K), demonstrating a high thermal stability. On the other hand, the substitution of Zr for Nb also improves soft magnetic properties of the Fe-based BMGs. The high saturation magnetization of 88 emu/g with a low coercivity of 20 Oe of the novel BMG alloys exhibit promising applications in magnetic industry.

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Environmental Performance of Fluorite Used To Catalyze MgO Reduction In Pidgeon Process

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Abstract. Environmental performances of fluorite used as catalyzer for chemical reaction between MgO and Si were investigated by performing pilot scale experiments of Mg production. F amounts of 0.012-0.116 kg were added in the charged briquettes and Mg slag generated from the chemical reaction in most of the tests weighted 4.26-4.96 kg with F contents ranging 0.21-2.52%. Based on high recoveries of F, 83-100%, in the slag after the reaction, it is estimated that there are little or no F compounds leaving the retorts during the pilot tests. However, high amount of F, 72.9 mg/kg, was leached out from an Mg slag sample obtained from an Mg plant, making it necessary to decrease amount of fluorite used as catalyzer for the reaction or to improve operation conditions, thus, enhancing rate for chemical reaction between MgO and Si in Pidgeon process.

Introduction

A steady growth of the world demand for magnesium (abbreviated as Mg) metal in the last 15 years [1, 2] has led to a rapid development for the Mg industry in China. In 2008, the Chinese output of primary Mg reached 630700 tons, accounting for 88.83% of the global Mg production [3]. Currently, there are more than 300 plants in China producing Mg by using Pidgeon process [3, 4].

The Pidgeon process was invented in 1940s by Pidgeon LM in Canada [5, 6]. It is a thermal process using silicon to reduce MgO from dolime at the temperature near 1200°C under vacuum pressure of 2-10 Pa inside retorts to generate Mg vapor, which then condenses at water-cooled end of the retorts forming crystalline Mg crowns. Fluorite, in a range of 2-3%, is usually added in the raw materials to catalyze the MgO reduction reaction [7-10].

Some environmental issues relating to the Mg production in China have been discussed in several studies [5-10]. Feng Gao et al. performed life cycle assessment of Chinese Mg production using Pidgeon process [9, 10]. Their studies showed that gaseous pollutants, including CO₂, SO₂, NO_x, CH₄ and HF, emitted from the production are main contributors to the accumulative environmental impact. The CO₂, SO₂, NO_x and CH₄ gases are emitted due to fuel combustions for the supply of process energy. The HF gas emission was related to fluorite consumed and it has been calculated that, for a fuel scenario using fluorite of 248 kg/ton Mg to catalyze the MgO reduction, HF gas of 34 kg/ton Mg could be emitted to account for 93% of the cumulative human toxicity potential [9], which poses threat to human health.

In some steelmaking processes fluorite can be added in slag as fluxing agent. Some of fluoride compounds with a high vapor pressure at the steelmaking temperature can be partially lost in the vapor phase [11, 12]. It is also possible for fluorine to leach out from the slag, causing a potential fluorine contamination to the ground water [13, 14]. Slag melting and leaching tests have been performed previously to examine mechanisms of fluorine evaporation and leaching from some types of steelmaking slag [11-14].

The methodology used to study the steelmaking slag [11-14] was adopted in our early work to examine fluoride emissions from Mg production [15]. The work included both pilot experiments of the Mg production using Pidgeon process and computer calculations of reaction products formed under the process conditions using FactSage 6.2. The results obtained indicated that 90% of the F in the added fluorite remained in the solid waste product discharged from the retorts, the Mg slag. [15].

The present work continues to investigate environmental performances of fluorite, with a wider range of fluorite addition in raw materials for the Mg production than the range for the early pilot experiments [15]. Results from the new tests are evaluated together with the results of the early work [15] to aid discussions on environmental impacts of fluorite used in the Pidgeon process.

Experimental

Experimental Materials. An Mg factory in northwest China provided raw materials used to make briquettes for the present pilot tests: dolime with MgO of 31% (mass fraction, the same below), ferrosilicon (FeSi) of Si 75% and fluorite of CaF_2 95%. A slag sample from the Mg production was also obtained from the factory for characterizations.

Apparatuses and Procedure for the Early and Present Pilot Tests. Two retorts (1 and 2 in Fig. 1) were made of heat resistant steel to simulate industry Mg production in Pidgeon process. Working sections of the retorts, with length of 760 mm and inner diameter of 159 mm, were inserted inside a muffle furnace (8 in Fig. 1) through two openings in front door of the furnace (7 in Fig. 1). A control box connected to a thermocouple inside the furnace adjusts furnace power (maximum 13 kW) to heat the working sections of retorts for MgO reduction. There are cooling water tubes (5 in Fig. 1) supplying water to the water cooling jackets near end sections of the retorts outside the furnace and vacuum pipes (4 in Fig. 1) connecting the outer, cooling ends of retorts to a vacuum system (6 in Fig. 1). The system consists of a filter and two vacuum pumps connected in series, producing a vacuum of around 10 Pa inside the retorts.

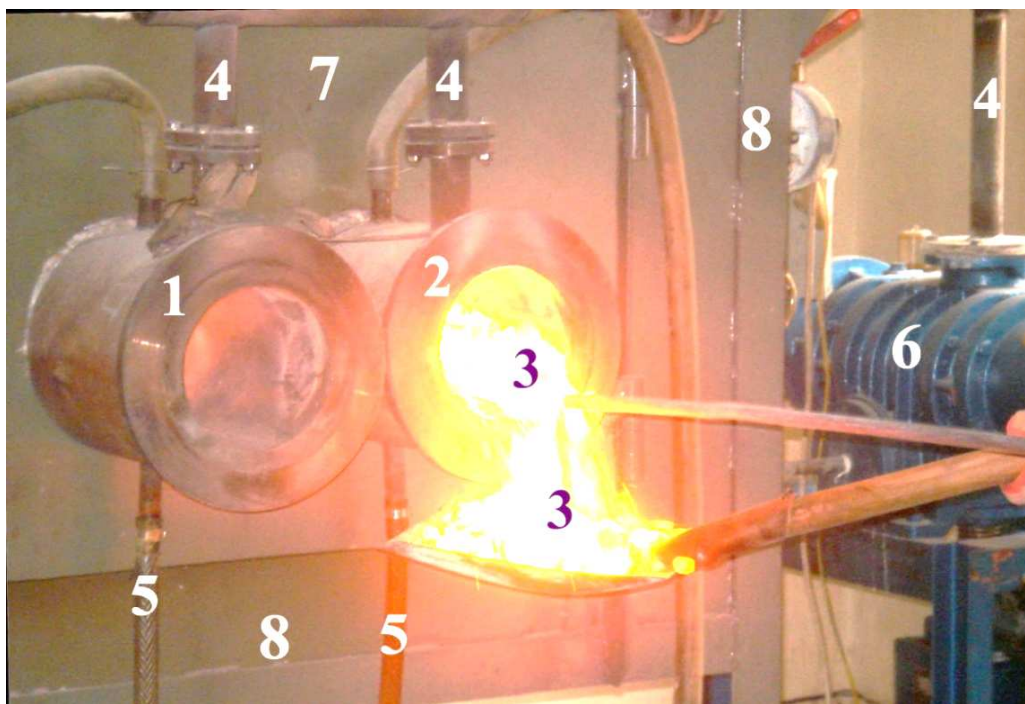


Fig. 1 Picture of set-up for pilot tests of Mg production using Pidgeon process: 1 and 2. Retort 1 and 2 with working section inside and water cooling jacket outside the muffle furnace, 3. Mg slag discharged from resort 2 at the end of a pilot test, 4. Vacuum pipes, 5. Cooling water tubes, 6. Vacuum system, 7. Front door of muffle furnace, 8. Muffle furnace

The materials for the pilot tests, dolime, ferrosilicon and fluorite, were ground to fine powder and then mixed thoroughly. The mixtures were pressed in a steel mould to make briquettes with sizes similar to the briquettes used for Mg production by the factory.

The briquettes with a weight ranging 5.6-10 kg for the pilot tests were charged in each of the retorts while the furnace temperature having reached to 1130°C. After the briquette charging, the flow rate of the water supplied in the cooling jacket increased to 30-40 L/min and the vacuum pumps operated to decrease retort pressure to 10 Pa. The vacuum of 10 Pa and temperature level of 1200°C were maintained in 4.5 hours for the MgO reduction. The vacuum pumps operated near 8 hours, similar to working periods of vacuum systems for the industry-scale Mg reduction [8, 15].

After the pilot tests, products of the MgO reduction, Mg ingot, materials from the retort zone for K and Na gas condensation and the production waste, Mg slag, were removed for cooling first and then for weighing and sampling at room temperature. At the time of discharging from the retorts, the temperature of Mg slag was still rather high and may be higher than 1000°C, estimated according to color of the slag, (3 in Fig. 1). Some other details of the pilot tests can be found in [15].

The contents of fluorine in the samples obtained from the pilot tests and the Mg factory were analyzed by SX380F-1 Microcomputer-based pF Ion Meter (Shanghai Dapu Instrument Co., Ltd. Ion-selective electrode method, GB/T 6730.28-2006). Some of the slag samples were also characterized by a SHIMADZU XRD-6000 diffractometer.

Results from the Pilot Tests and Discussion

Results of XRD Analyses of Mg Slag Samples from a Pilot Test and the Mg Plant

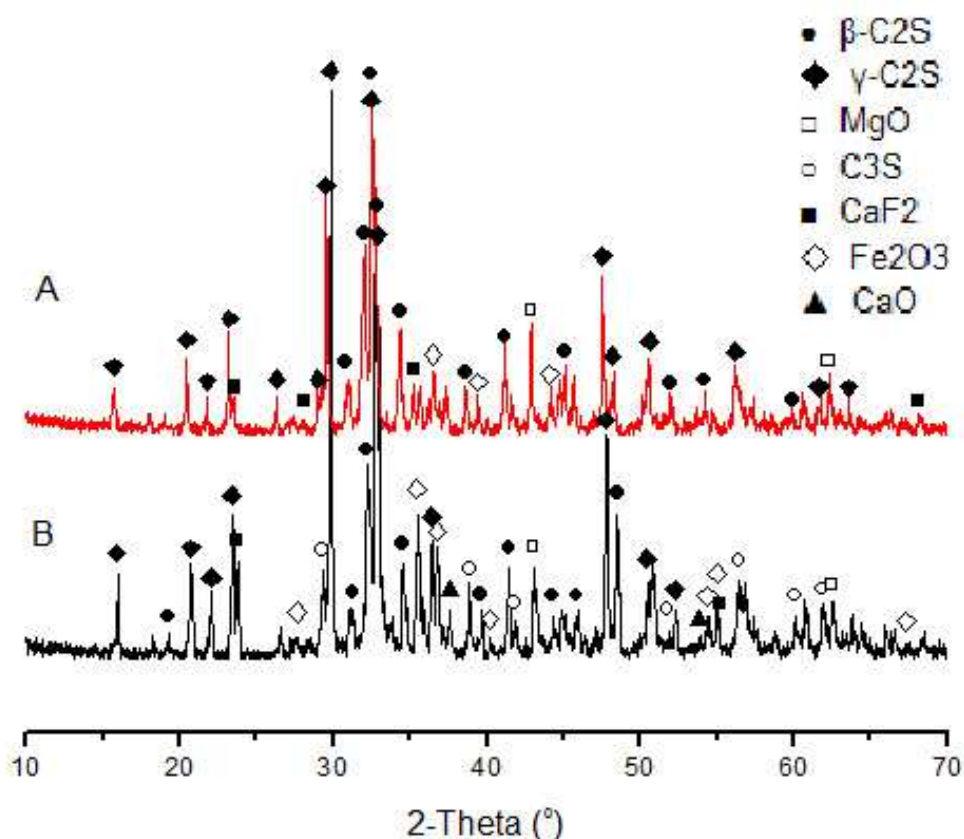


Fig. 2 XRD pattern of Mg slag sample from a pilot test (A) and the Mg plant (B)

XRD patterns in part A and B of Fig. 2 show γ -C₂S (γ -Ca₂SiO₄) and CaF₂ existing as a major and a minor phase, respectively, in Mg slag samples from a pilot test (A) and the Mg plant (B). The similar characters of minerals formed in both samples indicate that the pilot tests have closely simulated the industry scale Mg production using Pidgeon process. The CaF₂ phase may be near 5% in the slag samples from both the pilot test and the Mg plant according to the XRD results in Fig. 2.

F Contents in Input and Output Materials for the Early Pilot Tests [15]. Following test products were obtained from the early pilot test: Mg ingots of 0.8-1.85 kg (Mg contents of 92-98%), K and Na condensates of 23-61 g and Mg slags of 4.1-8.3 kg, as seen in Table 1.

In each of the 4 early tests, fluorite of 0.25 kg was added, but amounts of dolime and FeSi were lower in briquette materials for test 1 and 2 than for test 3 and 4, Table 1. Fluorite contents in the briquettes for test 1 and 2 are 4.1% and 4.5%, respectively, and higher than that for test 3 and 4, 2.5%. F contents in Mg slag from test 1 and 2 are thus 2.6 and 2.95%, respectively, and higher than F contents of 1.24-1.57% in the slag from test 3 and 4, Table 1. F contents of Mg ingots and K and Na condensates from test 1 and 2 are also higher. These results demonstrate a close relation between the F contents in solid products from the tests and fluorite amounts added in briquettes charged in the retorts.

Table 1 Weight data of input (briquettes) and output (products) materials for the early pilot tests and F contents analyzed in the products, % (weight percent)

Test No	Briquette materials [kg]			Products from test [kg]			F content in products [wt%]		
	Dolime	FeSi	Fluorite	Mg slag	Mg ingot	K and Na condensate	Mg slag	Mg ingot	K and Na condensate
1	5.0	0.84	0.25	4.1	0.9	0.031	2.6	0.064	0.169
2	4.5	0.84	0.25	4.2	0.8	0.023	2.95	0.042	0.166
3	8.13	1.67	0.25	7.1	1.8		1.57	0.022	—
4	8.13	1.67	0.25	8.3	1.85	0.061	1.24	0.047	0.07

Table 2 Results of F balance calculated using the data in Table 1 for input and output materials of the early pilot tests

Early pilot test		1	2	3	4
Input of F [g]	In briquettes	115.7	115.7	115.7	115.7
	In Mg slag	106.6	123.9	111.47	102.92
Output of F [g]	In Mg ingot	0.58	0.34	0.4	0.87
	In K and Na condensate	0.05	0.04		0.04
	Total F-output	107.23	124.28	111.87	103.83
(F-output)/(F-input) [%]		92.68	107.42	96.69	89.74
(F in Mg slag)/(F-input) [%]		92.13	107.09	96.34	88.95

Table 2 lists results of F balance computed by using the data in Table 1. In each of the 4 tests, there is the same amount of F-input, 115.7 g, in the briquettes. Amounts of F-output in the solid products included 103-124 g F in Mg slag, 0.34-0.87 g F in Mg ingots and 0.04-0.05 g F in K and Na condensates. The Mg slag contains more than 99% of the total F-output. Whereas, the weight sum of F in Mg ingots and in K and Na condensates is only less than 1% and can thus be ignored in the F-balance calculations. The simplification, using only the F amount in Mg slag to compute F balance, produces very small errors as indicated by the results in the last two rows in Table 2.

The results of F balance calculations in Table 2 demonstrate that 90-100% of F-input in the briquettes remain in the Mg slag obtained from the 4 early pilot tests. (A value of 100% is assumed for test 2.) Amounts of fluoride compounds leaving the retorts in gas form may thus be near none or very low in the 4 early tests.

F in Input Materials and Output Mg Slag for the Present Pilot Tests. Amounts of F added in briquettes ranged 0.012-0.116 kg in the present pilot tests. The weights of Mg slag obtained from most of the test chargers are 4.26-4.96 kg. F contents analyzed in Mg slag are between 0.21 and 2.52%. These data are presented in Table 3 and used in Equation 1 to calculate recovery of F in Mg slag from F added in the charged briquettes. The F recoveries for a half of the Mg slag samples from the present pilot tests are between 91.2 and 107%. For the other half of the slag samples, the F recoveries range 82.8-88.6%, see Table 3.

Recovery of F in Mg slag, % =

$$\frac{F \% \text{ analyzed in Mg slag} \times \text{Weight of Mg slag (kg)}}{F \text{ input in briquettes (kg)}} \times 100 \quad (1)$$

Table 3 F in input charges (briquettes), output Mg slag and computed recovery of F in Mg slag obtained from the present pilot tests of Mg production using Pidgeon process

Code of input charges for present pilot test	Input in briquettes		Output from the tests		Recovery of F in Mg slag [wt%]
	CaF ₂ , [kg]	F, [kg]	Mg slag, [kg]	F content in Mg slag [wt%]	
2011-11-16Y	0.075	0.035	4.26	0.68	83.5
2011-11-16F	0.075	0.035	4.96	0.72	102.9
2011-11-17Y	0.25	0.116	4.56	2.52	99.3
2011-11-17F	0.25	0.116	4.36	2.42	91.2
2011-11-20Y	0.125	0.058	4.86	1.13	94.9
2011-11-20F	0.05	0.023	4.96	0.46	98.6
2011-11-21Y	0.125	0.058	4.66	1.1	88.6
2011-11-21F	0.05	0.023	4.76	0.49	100.8
2011-11-22Y	0.125	0.058	4.66	1.08	87.0
2011-11-22F	0.025	0.012	4.56	0.21	82.8
2011-11-23Y	0.125	0.058	4.56	1.1	86.7
2011-11-23F	0.025	0.012	4.76	0.26	107.0
2011-11-25Y	0.25	0.116	7.26	1.41	88.5
2011-11-25F	0.05	0.023	8.26	0.24	85.7

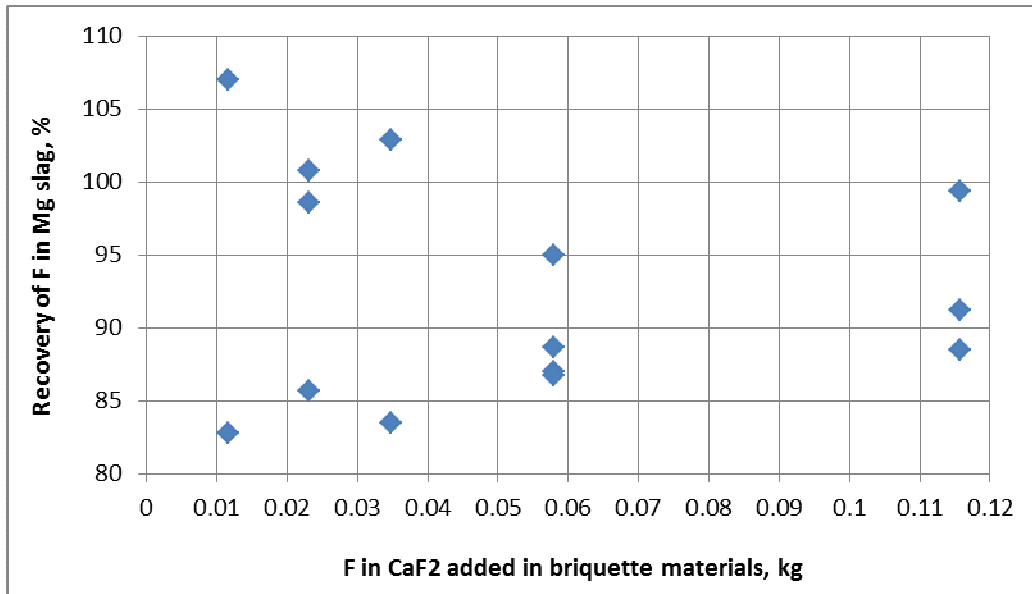


Fig. 3 F recoveries in Mg slag versus F amounts in CaF₂ added in input briquette materials for the present pilot tests

Figure 3 shows a wider spreading of the F recovery values, 82.8-107%, for the tests with F amounts less than 0.04 kg added in the briquette materials. The lower F amounts may give rise to larger errors from slag sampling and F analyzing, leading to the wider spreading of the F recoveries. Increases of F addition to amounts higher than 0.05 kg decrease the errors and the recovery value span. While the added F amount reaching to 0.116 kg in 3 of the present pilot tests, the F recoveries are 88.5-99.3%, which are very similar to the F recoveries, 90-100%, calculated for the 4 early pilot tests, Tables 2 and 3 and Fig. 3.

The FactSage computation predicts that gaseous CaF and CaF₂ can form to a greater extent from the charged CaF₂ in the working section of a retort at the temperature ranging 1100-1200°C [15]. While leaving the working section, the gaseous fluorides will condense back to solid CaF₂ near the end section of the retort, where Mg gas is cooled to around 500°C to form crystalline Mg crown [15]. The water cooling jackets with water supplied by the tubes (5 in Fig. 1) cool the end section and make it impossible for the F compounds to leave the retort through the end section in gas form.

Gao et al. calculated that around 30% of F in fluorite emitted as gaseous pollutant, HF, from Pidgeon process using fluorite as a catalyzer [9, 10]. For the HF formation not only fluorite but also some water should be present in the retorts at the temperature higher than 600°C [16-18]. There is normally no crystallized water in the briquettes and any water entering the retort during the briquette charging will leave as H₂O gas well below the temperature for the HF gas formation. It is thus clear that two important factors, not water input in retorts and a cooling of the gaseous compounds near the end of retort, must be taken into account for an accurate computation of fluoride emissions from Pidgeon process.

Besides, the waste briquettes, 3 in Fig. 1, at the beginning of discharge from the retorts, are seen still with rather high temperature, which may be near the gasification temperature for F compounds. However, observations on briquette discharging after the reduction in some of the pilot tests indicate that the briquette color changed from the red-yellow at the beginning to the color of room temperature in the time of less than 5 minutes. 7-9 minutes after discharging some briquettes started to disintegrate confirming the briquette temperature ranging 500-600°C with occurrences of β - γ phase transformation of C₂S and the γ -C₂S-driven slag/briquette disintegration. It is estimated based on the observations that the period with suitable temperature may be too short for the F compounds to gasify and, thus, little or no F compounds leave the briquettes after the discharging.

Some of fine particles of fluoride compounds may leave the retorts together with other solid particles of small size from the briquettes. A part of the solid particles may be captured by the filter before the vacuum system or deposited in the vacuum system, 6 in Figure 1.

Results in Tables 2 and 3 indicate that F recoveries are somewhat less than 100% in the Mg slag obtained from some of the early and present pilot tests, which may be due either to existences of experimental errors or to the losses of F compounds in the vacuum system and from the gasification at the briquette discharging. Some further work may be needed to quantify these small losses of F compounds.

F leaching from a Slag Sample from the Mg Plant. A slag sample containing CaO of 53.71%, SiO₂ of 31.02%, MgO of 3.92% and F of 1.53% from the Mg plant was used for a leaching test, which was performed with liquid-solid ratio (L/S) of 10 according to EN 12457-2 [20]. This test is one of the methods to characterize materials for the acceptance of wastes in landfills pursuant to Directive 1999/31/EC11 [21]. A waste material is generally considered as environmentally friendly for using as building material if its element leaching values are lower than the limit values set for the inert waste by the Directive.

The Mg slag leached out 72.9 mg/kg F, which is higher than 10 mg/kg, the limit value set for F leaching from inert waste pursuant to Directive 1999/31/EC11 [21]. The Mg slag may thus not be suitable to use as an environmentally sound building material due to the high value of F leaching and a higher risk for a potential fluorine contamination to the ground water.

Suggestions to Avoid Environmental Impact of Fluorite Used for Mg Production. The Mg slag of 6 tons is generated to produce one ton of Mg ingots by the Pidgeon process [7, 8]. An Mg slag recycling as building materials is important for saving valuable natural resources and decreasing the global warming impact. However, the early and present studies show that the fluorite used to catalyze MgO reduction will largely remain in the Mg slag, giving high risk for a potential fluorine contamination of ground water. Furthermore, there may also be risks for gaseous fluoride emission while the Mg slag is burned as one type of clinker raw materials for cement production [7].

It is thus necessary to carry out research work to improve operation conditions for the MgO reduction and, hence, to decrease amounts of fluorite used as catalyzer. It may also be needed to develop some techniques for stabilizations of fluoride compounds in the Mg slag [11-14].

Conclusions

In order to clarify environmental performances of fluorite used as catalyzer for silicothermic reduction of MgO, the present work is undertaken, performing pilot scale experiments to produce Mg by Pidgeon process. Results from the study include:

1. F amounts ranging 0.012-0.116 kg were added in briquettes in the present pilot tests. The weights of Mg slag obtained from most of the test chargers are 4.26-4.96 kg with F contents of 0.21-2.52%.
2. Values of recovery of F in Mg slag from F added in the charged briquettes are calculated. The F recoveries for 50% of the Mg slag samples from the present pilot tests are 91.2-107%. For the rest of the slag samples, the F recoveries range 82.8-88.6%. The high rates of F recovery indicate little or no F compounds leaving the retorts during MgO reduction.
3. XRD studies indicate CaF_2 existing as a minor phase in the Mg slag samples from both a pilot test and the Mg plant. The similar characters of minerals found in both laboratory and plant samples indicate that the pilot tests have closely simulated the industry scale Mg production using Pidgeon process.
4. Leaching test was performed using an Mg slag sample from an Mg plant in China with liquid/solid ratio of 10 according to EN 12457-2. The leaching of F from the Mg slag is 72.9 mg/kg, higher than 10 mg/kg, the limit value set for F leaching from inert waste pursuant to Directive 1999/31/EC11.
5. Due to the risk for a potential F contamination to the ground water, it is not suitable to use the Mg slag as an environmentally sound building material. It is thus necessary to decrease amount of fluorite used as catalyzer in the Pidgeon process.

Acknowledgements

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Study on low-temperature oxidation's endothermic character of coal with comparative-oxidation method

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Key words: coal; Low-temperature oxidation; Heating rate

Abstract: In this paper air was passed through into one progress temperature-controlled box with coal sample and nitrogen into another as comparison during the procedure of coal's low-temperature (10~80°C) oxidation. Draw the heating curves and heating rate curve, and equation model is built combined with energy conservation, then concludes the heat release rate of the coal samples in the air conditions. The experimental results show that the condition with air is more close to the storage conditions of coal such as transportation in reality, which is very significant to prevent the spontaneous combustion of coals.

Introduction

As we all know, our coal resources are very rich, the output and consumption of coal in China is premier in the world, and it occupies about 75 percent of the internal primary energy output and total consumption. However, conflagration caused by the spontaneous combustion of coal is very severe. Coal spontaneous combustion seriously threatens the mining, transportation, storage of coal; therefore, it is of significance to study spontaneous combustion. The Low-temperature oxidation of coal is a inevitable stage of coal spontaneous combustion, but in low temperature the reaction is very slow, with small quantity of heat, which make it difficult to appreciate and to prevent conflagration caused by the spontaneous combustion.

The experiment process

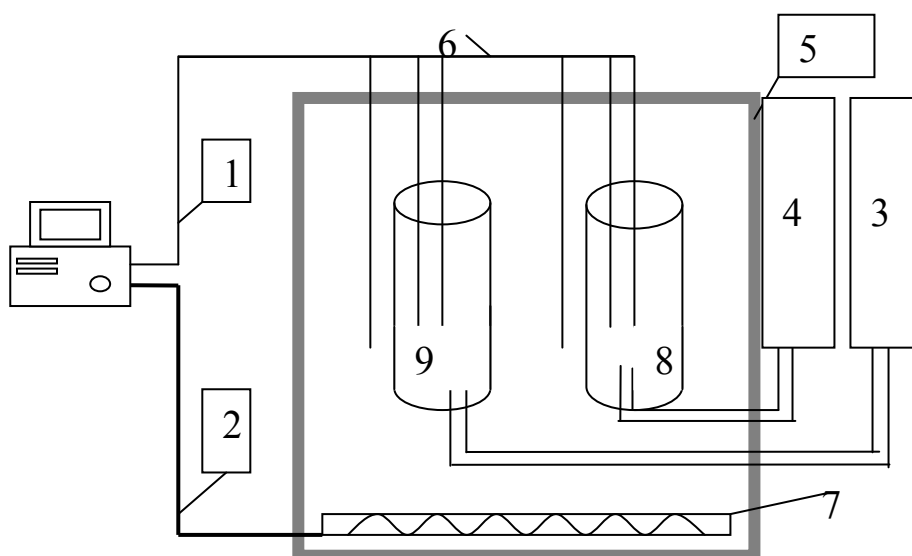


Figure 1 Experiment device figure

- 1- Temperature gathering 2- Heating control 3- Nitrogen gas heating dry device
4- Air heating drying equipment 5- Program control heating box 6- Thermocouple group
7- Heater 8- Coal samples 1 9- Coal samples 2

Place two coal samples cans in heating-controlled box side by side, cylindrical coal sample cans ' height is about 35 cm, radius 6 cm. Two coal sample cans full of coal are inserted two thermocouples in the same place, the middle height place where $r = 0$ and $r = 3$ cm. Coal samples1 are flowed into the air near the center position, flow rate is 5.5 ml/min. coal samples2 enter nitrogen, flow rate is 5.5 ml/min. The heating control for the experiment is each hour 2 °C. The device is shown as the figure 1 below.

Experimental results

Experiment with coal sample from the same place under the same conditions as shown in figure 1 for two times,
The results are as follows:

The experimental results are as follows(T =temperature; t =time; H =Heating rate):

The first experiment

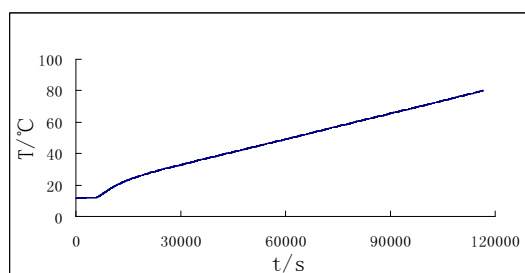


Figure 2 (a) The coal sample into the air heating curves

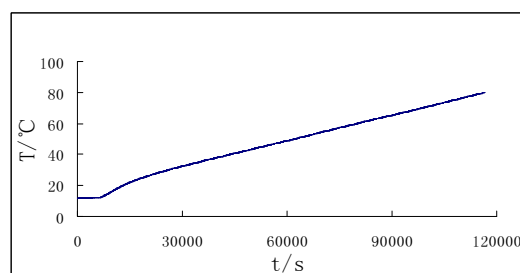


Figure2(b) Ventilation with nitrogen gas heating curves of coal samples

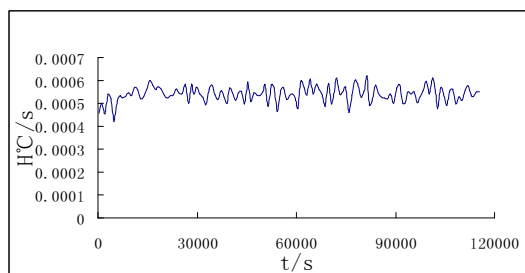


Figure 3 (a) The coal sample into the air heating rate chart

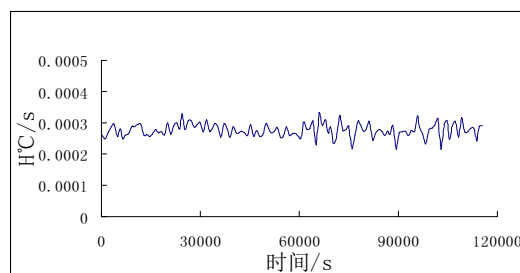


Figure 3 (b) Ventilation with nitrogen gas coal samples heating rate chart

- 1) It can be seen the coal sample in the ventilation with nitrogen is slower in increasing temperature from figure2(a), figure2(b); From figure 3 (a)and figure 3 (b) we can see the rate increasing temperature of coal samples through into the air and ventilation with nitrogen is 0.00055 °C / s, 0.00025 °C / s. Since the experimental conditions is consistent, so we can calculate the heating rate of the coal samples in air environment ,that is 0.0003 °C / s.

The second experiment

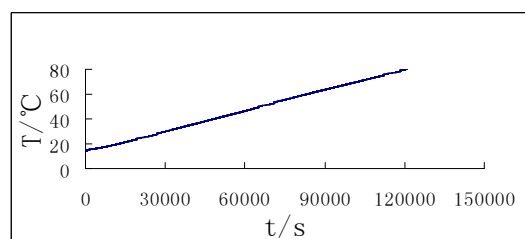


Figure 4 (a) The coal sample into the air heating curves

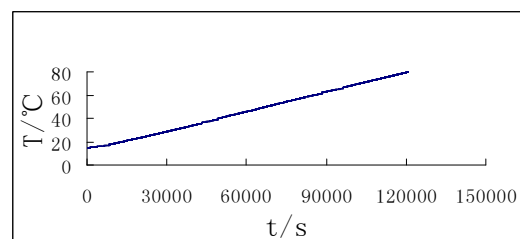


Figure 4 (b) Ventilation with nitrogen gas heating curves of coal samples

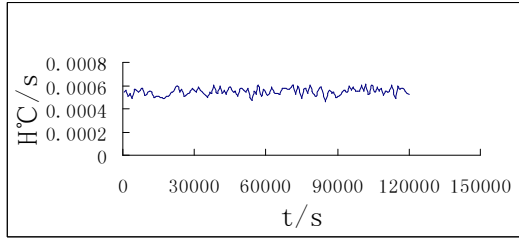


Figure 5 (a) The coal sample into the air heating rate chart

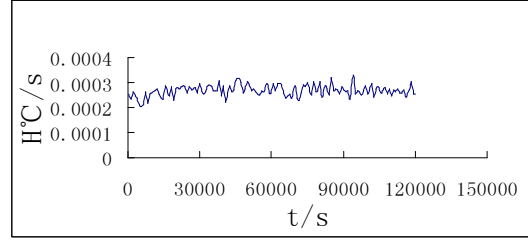


Figure 5 (b) Ventilation with nitrogen gas coal samples heating rate chart

2) From figure 4 and figure 5 we can see the rate increasing temperature of coal samples through into the air and ventilation with nitrogen is 0.00057°C/s, 0.00027°C/s. Since the experimental conditions is consistent, so we can calculate the heating rate of the coal samples in air environment, that is 0.0003 °C / s.

3) When through the coal sample into gas, its internal has energy balance, and because of the gas flow rate is very small, so the quantity of heat that use up by convection can be ignored, the equations :

The thermal equilibrium when entering the air is:

$$\rho_{coal} C_{coal} \frac{\partial T_1}{\partial t} = -\lambda \frac{\partial^2 T_1}{\partial x^2} + Q_{gen} - H_w \frac{dC_w}{dt} \quad (1)$$

Among the among the rest, ρ_{coal} : the density of coal samples, kg/m³; C_{coal} : specific heat capacity of coal, J / (kg, K); T_1 : the temperature of coal sample into the air K; t : time, s; x : distance, m; λ : the thermal conductivity, W / (m•K) ; H_w : wet heat or water evaporation heat unit volume and unit moisture, J/(mol•m³); C_w : moisture content, mol, Q_{gen} : coal heat production for oxidation, W.

The thermal equilibrium when entering the nitrogen is:

$$\rho_{coal} C_{coal} \frac{\partial T_2}{\partial t} = -\lambda \frac{\partial^2 T_2}{\partial x^2} - H_w \frac{dC_w}{dt} \quad (2)$$

T_2 : the temperature of coal sample when entering nitrogen, K.

calculate the heating rate of the coal samples according to figure(1), figure(2):

$$Q_{gen} = \rho_{coal} C_{coal} \frac{\partial (T_1 - T_2)}{\partial t} + \lambda \frac{\partial^2 (T_1 - T_2)}{\partial x^2} \quad (3)$$

choose ρ_{coal} : 1.1g/cm³; C_{coal} : 1.1kJ/ (kg • K); λ : 2.13W (m•°C)。

Combined the experimental data with equilibrium (3), the second smaller equation of the right hand can be ignored, conclude the heat production rate of coal samples: 0.363 kw/m³

Conclusion

(1) Of coal samples for 10 ~ 80 °C temperature control program temperature experiments, the air and are the ventilation with nitrogen experiments, two conditions respectively the heating rate is about 0.00055°C/s, 0.00025°C/s.

(2) Combined with coal sample temperature curve and heating rate curve, coal sample set up the heating rate model, have to produce hot rate equations, that heat production rate of coal samples 0.363kw/m³.

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Thermodynamic Research of Inclusion Forming in FeSiB Alloy based on Energy Materials

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Keywords: inclusion; oxide; nitride; FeSiB alloy, energy materials

Abstract: The thermodynamic analysis shown that oxygen content in master alloy is very low, so other alloy elements content which are balance to oxygen are relatively high. In the amorphous master alloy, deoxidizing capacity of silicon is stronger than boron, and with process of decrease of the temperature, oxygen content decrease. The silicon in the master alloy can also take off the oxygen content below 1 ppm. Denitrification capacity of boron is stronger than silicon, and with process of decrease of the temperature, nitrogen content decrease. The boron in the master alloy can also take off the nitrogen content below 4 ppm. All of the research are based on energy materials and it will be useful for the development for energy saving.

Introduction

Amorphous strip is very thin, the higher the cleanliness, the performance is better. The strip surface quality and the quality of the master alloy make a big difference. The inclusions in the master liquor with high content would cause amorphous strip to contain inclusions and may lead to appear micro pores or cracks [1~3]. Along with the development and improvement of metallurgical technology, the cleanliness requirements of the alloy strips increase continually, so the requirements of the inclusions in the amorphous master alloy are much stricter. Analysis of the formation mechanism of inclusion, the research of the formation conditions, and then control of its formation or effective removal, is very important to improve cleanliness of the amorphous master alloy.

B is an active element. If unprotected boron was added to the high temperature liquid iron, nitrogen and oxygen will react with boron to form boron nitride and boron oxide [4]. Because the master alloy component is different from the conventional steels, the silicon and boron content is very high, the main composition is $w[\text{Si}]=5.4\%$, $w[\text{B}]=2.6\%$, $w[\text{C}]=0.01\%$, so the oxygen, nitrogen content in the master alloy can be removed very low.

1. Formative conditions for oxide.

The silicon and boron content in the amorphous master alloy is higher, they has the function of deoxidizer, and the ability is strong, so we can judge balance oxygen content in the master alloy is very low by qualitative, and inclusions in the concretionary master alloy is very few [5~6].

Silicon and boron in the master alloy can deoxidize, the reaction that element combines with oxygen to generate inclusion is commonly.

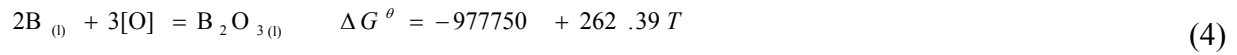
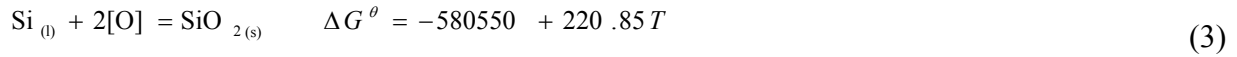


In the Equ(1), M is the deoxidizing elements, the balance constant K_M of the reaction is shown in the Equ(2).

$$K_M = \frac{a_{M_xO_y}}{[a_M]^x [a_O]^y} \quad (2)$$

When deoxidizing products is pure oxide or is saturated state, $a_{M_xO_y}=1$. We can use K_M to judge elements deoxidizing capacity and residual oxygen content in the steel. The greater the K_M , explain the stronger ability of deoxidizing, the less residual oxygen content in the steel.

The reactions of silicon, boron and oxygen are shown in Equ(3) and Equ(4).



Reaction Gibbs free energies are shown in Equ(5) and Equ(6).

$$\Delta G = \Delta G^\theta + RT \ln\left(\frac{a_{\text{SiO}_2}}{a_{\text{Si}} \times (a_{\text{O}})^2}\right) = -580550 + 220.85 T + RT \ln\left(\frac{1}{a_{\text{Si}} \times (a_{\text{O}})^2}\right) \quad (5)$$

$$\Delta G = \Delta G^\theta + RT \ln\left(\frac{a_{\text{B}_2\text{O}_3}}{(a_{\text{B}})^2 \times (a_{\text{O}})^3}\right) = -977750 + 262.39 T + RT \ln\left(\frac{1}{(a_{\text{B}})^2 \times (a_{\text{O}})^3}\right) \quad (6)$$

SiO_2 , B_2O_3 generated are pure oxides, $a_{\text{SiO}_2}=1$, $a_{\text{B}_2\text{O}_3}=1$. Oxygen content in the master alloy is very low, $w[\text{O}]=a_{\text{O}}/f_{\text{O}}$, f_{O} is determined by component content of master alloy and interaction coefficient, a_{Si} and a_{B} are determined by melt activity model. When silicon and boron deoxidization reaction reach to balance, the oxygen contents are shown in Equ(7) and Equ(8).

$$w[\text{O}] = \frac{1}{f_{\text{O}}} \sqrt{\frac{1}{a_{\text{Si}}} \cdot e^{\frac{-580550 + 220.85 T}{RT}}} \quad (7)$$

$$w[\text{O}] = \frac{1}{f_{\text{O}}} \sqrt[3]{\frac{1}{(a_{\text{B}})^2} \cdot e^{\frac{-977750 + 262.39 T}{RT}}} \quad (8)$$

In the master alloy containing 5.4% silicon, the relationship of oxygen content and the temperature is shown in Fig.1. It is shown that oxygen content in the master alloy decreased while the temperature decreased, and it can be taken off to 1 ppm below in 1400°C. In the master alloy containing 2.6% boron, the relationship of oxygen content and the temperature is shown in Fig.2. It is shown that oxygen content in the master alloy decreased while the temperature decreased, and it can be removed to 2ppm below in 1400°C.

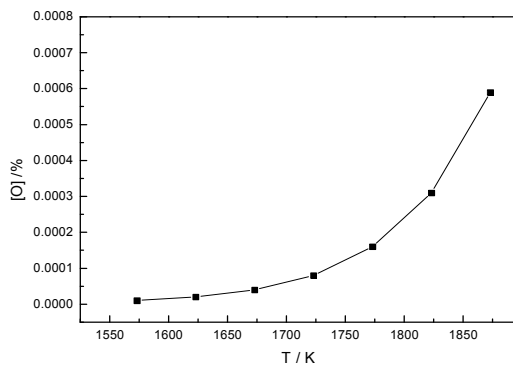


Fig.1 Oxygen content in alloy ($w[\text{Si}]=5.4$)

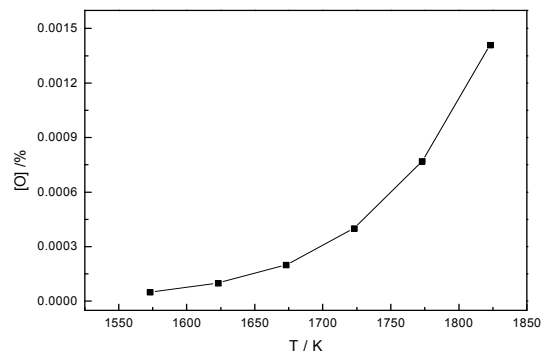


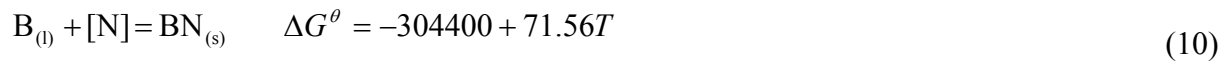
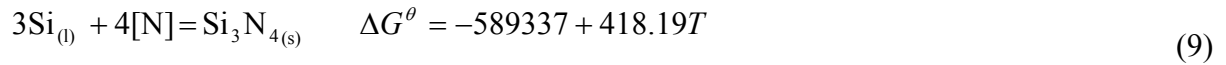
Fig.2 Oxygen content in alloy ($w[\text{B}]=2.6$)

2. Formative conditions for nitride

In conventional iron liquid, nitrogen is a more "stubborn" element, but in amorphous master alloys containing very high boron content are relatively easy to removal from the master alloy. The influence of nitrogen solubility in iron liquid of boron and silicon is not same, silicon and nitrogen are difficult to form compounds, but boron and nitrogen are easy to form compounds, so denitrification ability is very strong. The boron content in the amorphous master alloy is higher, so we can judge balance nitrogen content in the master alloy is very low by qualitative, and nitride inclusions in the concrectionary master alloy is very few.

It is similar to deoxidization reaction that silicon and boron in the master alloy can combine with nitrogen to generate inclusion.

The reaction of Silicon, boron and nitrogen are shown in Equ(9) and Equ(10).



Reaction Gibbs free energies are shown in Equ(11) and Equ(12).

$$\Delta G = \Delta G^\theta + RT \ln\left(\frac{a_{\text{Si}_3\text{N}_4}}{[a_{\text{Si}}]^3 \times [a_{\text{N}}]^4}\right) = -589337 + 418.19T + RT \ln\left(\frac{1}{[a_{\text{Si}}]^3 \times [a_{\text{N}}]^4}\right) \quad (11)$$

$$\Delta G = \Delta G^\theta + RT \ln\left(\frac{a_{\text{BN}}}{a_{\text{B}} \times a_{\text{N}}}\right) = -304400 + 71.56T + RT \ln\left(\frac{1}{a_{\text{B}} \times a_{\text{N}}}\right) \quad (12)$$

Si_3N_4 , BN generated are pure nitrides, $a_{\text{Si}_3\text{N}_4}=1$, $a_{\text{BN}}=1$, $a_{\text{N}}=f_{\text{N}} w[\text{N}]$. In the amorphous master alloy, deoxidizing capacity of silicon is stronger than boron, and oxygen content decreased with decreasing of the temperature. The silicon in the master alloy can also take off the oxygen content to 1 ppm below. Denitrification capacity of boron is stronger than silicon, and with process of decrease of the temperature, nitrogen content decrease. The boron in the master alloy can also take off the nitrogen content to 4 ppm below. a_{Si} and a_{B} are determined by melt activity model. When silicon and boron denitrification reaction reach to balance, the oxygen contents are shown in Equ(13) and Equ(14).

$$w[\text{N}] = \frac{1}{f_{\text{N}}} \cdot \sqrt[4]{\frac{1}{(a_{\text{Si}})^3} \cdot e^{\frac{-589337+418.19T}{RT}}} \quad (13)$$

$$w[\text{N}] = \frac{1}{f_{\text{N}} a_{\text{B}}} \cdot e^{\frac{-304400+71.56T}{RT}} \quad (14)$$

In the master alloy containing 5.4% silicon, the relationship of nitrogen content and the temperature is shown in Fig.3. It is shown that nitrogen content in the master alloy decreased while the temperature decreased, and it can be taken off to 8 ppm below in 1400°C. In the master alloy containing 2.6% boron, the relationship of nitrogen content and the temperature is shown in Fig.4. It is shown that nitrogen content in the master alloy decreased while the temperature decreased, and it can be removed to 4 ppm below in 1400°C.

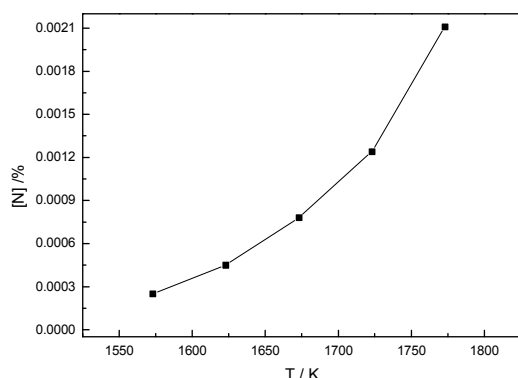


Fig.3 Nitrogen content in alloy (w[Si]=5.4)

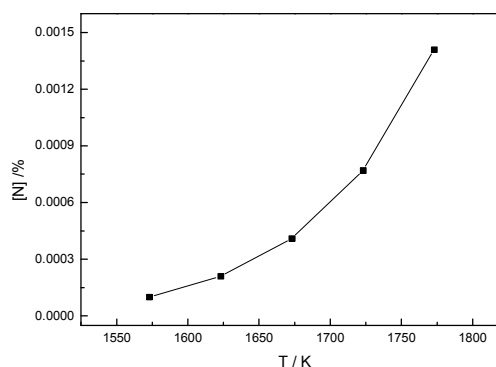


Fig.4 Nitrogen content in alloy (w[B]=2.6)

The theoretical calculation value represents the highest content of the harmful elements which is brought by the raw material. The traditional methods adopt boron iron to smelt amorphous master alloy, which bring into a lot of aluminum element and make aluminum content very high in the master alloy, and without slag absorption function, the formed aluminum oxide and titanium oxide inclusion is hard to be removed. The raw material of direct reduction method is boron anhydride, in which aluminum, titanium content is much lower than boron iron, and direct reduction method generate a large smelting slag, which can absorb inclusion well, so the inclusion generated in the master alloy is very less.

4. Conclusions

(1) In the amorphous master alloy, deoxidizing capacity of silicon is stronger than boron, and with process of decrease of the temperature, oxygen content decrease. The silicon in the master alloy can also take off the oxygen content below 1 ppm.

(2) Denitrification capacity of boron is stronger than silicon, and with process of decrease of the temperature, nitrogen content decrease. The boron in the master alloy can also take off the nitrogen content below 4 ppm.

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Neural Model of the Producing Process for Predicting Filtration Properties of Melt Blowing Nonwovens

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Keywords: melt blowing, nonwoven, filtration performance, processing parameter, artificial neural network model.

Abstract. The filtration properties of melt blowing nonwovens are affected by the pore structure of nonwovens which is strongly related to the processing parameters. However, it is difficult to establish physical models on the relationship between the processing parameters and filtration properties. In this work, the ANN model is established for predicting the filtration properties of melt blowing nonwovens from the processing parameters. The results reveal that the ANN method is really an effective and viable modeling technique. This method can exactly predict the filtration properties because the results are good enough.

Introduction

The melt blowing process [1-2], originally developed in 1950s, can produce nonwoven fabrics with microfiber structure. Fiber diameters can be as little as 1-10 μm , even 0.5 μm . The melt blowing nonwoven fabrics are highly efficient filter materials whose filtration efficiency can be over 99.9%. In the melt blowing process, a molten stream of polymer is extruded from the die and rapidly attenuated into microfibers by the air jet with high velocity and high temperature. The melt blowing nonwoven fabrics are characterized by high porosity, tiny pore diameter and ultrafine fibers, which make these fabrics well serve the function of high efficiency filter materials used in various fields. The melt blowing nonwoven fabrics has acted as the filtering materials for filtering out leukocytes from the transfusion blood to prevent the adverse reaction and speed of viruses. The filtration properties of melt blowing nonwoven fabrics are affected by the structure of nonwovens which is related to the processing parameters. However, it is rather difficult to establish a physics model to describe the process-property relation of melt blowing nonwoven fabrics.

In recent years, artificial neural network (ANN) model has been used in many engineering fields to predict material properties. Within the textile industry alone, numerous applications have been reported [3-4]. In the previous papers, many researchers found that prediction performance was the best for ANN model, followed by the statistical and physics models. It has been seen from the literature that predictions by ANN model have more promising results compared to conventional prediction methods such as regression or correlation analyses, especially for non-linear and complex relationships among system variables. In this paper, we attempt to predict filtration performance of melt blowing nonwoven fabrics with ANN model. The results show that processing parameters have an important effect on filtration performances.

Experimental procedure and results

Materials. The polymer used is S904 polypropylene with a melt flow index of 54.

Processing parameters. The experiments of melt blowing nonwovens equipment were carried out at our university. The melt blowing process parameters of concern were as following: the polymer throughput rate, air initial velocity, die-to-collector distance, air pressure, and number of layers etc., and the variation ranges of the parameters are 0.0015--0.0035g/min/hole, 90-198m/s, 8-14cm, 13-23 Pa, 4-15 layer, respectively.

Testing conditions. The experimental samples were subject to conditioning at 65% RH and $20 \pm 5^\circ\text{C}$ for 24 hours and then the testing was carried out.

Program and results. The filtration property under study is the filtration resistance. The experimental program and results are shown in Table 1.

Table1. Experimental program and results

No.	Polymer throughput rate (g/min/hole)	Air initial velocity (m/s)	Die-to-collector distance (cm)	Air pressure (Pa)	Number of layers (n)
1	0.0022	98	10	15.4	4
2	0.0016	143	8	13.8	6
3	0.0024	165	12	13.8	8
4	0.0028	198	14	14.2	10
5	0.0016	202	14	14.2	6
6	0.0016	89	12	15.4	8
7	0.0016	156	10	14.2	12
8	0.0016	178	14	19.8	11
9	0.0030	126	10	20.4	13
10	0.0022	134	8	23.0	10
11	0.0024	134	12	22.8	8
12	0.0028	148	14	18.6	6

Artificial neural network model

The artificial neural networks model with back-propagation learning scheme. Artificial neural networks [5] have been applied to different textile problems. Among many artificial neural network schemes, multi-layer feed-forward neural networks with back-propagation learning algorithms based on gradient descent have been widely used, since they offer unlimited approximation power for non-linear mapping. Therefore, in this study, an ANN was used with the back-propagation learning scheme to predict the filtration performances of melt blowing nonwoven fabrics. The back-propagation neural network is essentially a network of simple processing elements working together to produce a complex output. These elements or nodes are arranged into different layers as input, hidden and output. The output from a back propagation neural network is computed using a procedure known as the forward pass. The input layer propagates a particular input vector's components to each node in the hidden layer. Hidden layer nodes compute output values, which become inputs to the nodes of the output layer. The output layer nodes compute the network output for the particular input vector. The forward pass produces an output vector for a given input vector based on the current state of the network weights. Since the network weights are initialized to random values, it is unlikely that reasonable outputs will result before training. The weights are adjusted to reduce the error by propagating the output error backward through the network. This process is where the back propagation neural network gets its name and is known as the backward pass. The training set is repeatedly presented to the network and the weight values are adjusted until the overall error is below a predetermined value. Since the Delta rule follows the path

of greatest decent along the error surface, local minima can impeded training. The momentum term compensates for this problem to some degree. One of the most crucial aims of the back propagation network is to minimise the error function by using the gradient steepest descent method. The error function is:

$$E = \frac{1}{2} \sum_k (Y_{dk} - Y_k)^2 \quad (1)$$

where Y_{dk} is the desired output and Y_k is the calculated output value of the output layer, respectively.

The weights updated themselves by using error function as:

$$\Delta w_{ij} = -\eta \frac{\partial E}{\partial w_{ij}} \quad (2)$$

Here is the learning rate and determines the performance of the learning capability of network and w is the weight. Sigmoid function was used as activation function in this study. Sigmoid function is as follows:

$$f(x) = \frac{1}{1 + e^{-x}} \quad (3)$$

In this work, three layered network structure was used which composed of input hidden and output layers. The learning rate and momentum were optimised at 0.1 and 0.8, respectively. The model built in this study can be seen in Figure 1.

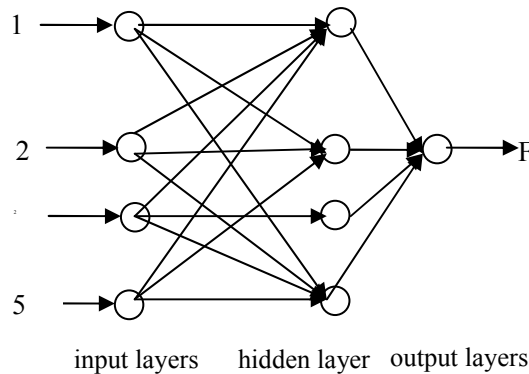


Fig. 1 Structure and architecture of an ANN model

Back-propagation algorithm. In the ANN structure, all the neurons in one layer are connected to neurons in the next layer. The error between the correct output and the ANN output is minimised using the back-propagation learning method. The structure of ANN is given in Figure 1, and the back-propagation algorithm is briefly explained in the following steps. The algorithm has five steps: (1) A training set containing known input-output pairs is defined. (2) All the weights, w_{ij} are arbitrarily assigned at the first iteration. (3) At each layer of the network, the outputs of the neurons are calculated in a forward direction. (4) At the output layer, the output of the ANN was compared to the given target values in the training set, resulting in an error term. (5) This error term is back-propagated through the network by updating the weights according to a desired algorithm. The program continues for a given number of iterations, or until an accepted error is achieved.

Practicing model. We use 10 groups of datum as direct practice and 2 groups as test and verification. The algorithm of model is momentum regulation and the reading ratio is adjusted to itself. When the BP network is being practiced, its parameters could be defined according to the structure. The number can be defined according to the deviation produced in practice on every neural unit of BP.

The practice results shows that the optimal number of units in hidden layer is equal to the average of unit number in output layer and input layer. Therefore, the practice time could be shortening and the precise prediction result could be output.

Result and discussion.

As above mentioned, the deviation of specimen is 0.000102 after the BP network running 3000 times. The compare of analogy value to actually experimental value in practice group, as well as the compare of predictive value to actually experimental value in test or verification group in the light of BP network, is shown in Table 2. The prediction result shows that BP network can predict

Table 2. Results of BP practice and prediction

No.	Practice output (Filtration resistance) (Pa)	Actual output (Filtration resistance) (Pa)	Error (%)
1	1.7756	1.78	-0.2472
2	1.9842	1.98	0.2117
3	1.5459	1.56	-0.9121
4	3.1101	3.10	0.3247
5	2.6698	2.67	-0.0200
6	2.8614	2.86	0.0489
7	4.0267	4.02	0.1664
8	4.2311	4.23	0.0260
9	3.2245	3.22	0.1396
10	2.0819	2.08	0.0913
11	2.3386	2.34	-0.0600
12	3.4241	3.42	0.1197

filtration properties of melt blowing nonwovens fabrics well for the result is rather exact. Meanwhile, the coincidence of study practice specimen is good as well as the predictive value of two-test and verification specimen groups approximates to their experimental value.

Summary

We use the ANN model to predict filtration properties of melt blowing nonwoven fabrics. Our findings indicate that the filtration properties of melt blowing nonwoven are determined by the polymer throughput rate, air initial velocity, die-to-collector distance, air pressure, and number of layers etc. The predicted and experimental values agree well, indicating that the neural network is an excellent method for predictors. On the basis of the results obtained, with the help of the ANN model analysis, we can predict the filtration properties of melt blowing nonwoven fabrics easily and accurately.

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An Analysis on Energy-saving Generation Dispatch Considering Carbon Emission Limitation and the Development of New Energy Materials

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Key words: energy materials, renewable energy, energy-saving generation dispatch, carbon reduction

Abstract: The development of new energy materials offers a solid foundation for the expansion of renewable and other clean energy such as onshore/offshore wind energy, solar energy, biomass and nuclear energy. With the rapid growth of the installed capacity of these clean energy types, it is urgent to further improve the generation dispatch mode to guarantee the grid connection. An energy-saving generation dispatch model is established to find out the optimal unit commitment of thermal power and other clean power, with a consideration of carbon emission limitation.

1. Introduction

China is now facing a great challenge in balancing its rapid economic growth and energy and environment sustainability. Reducing energy intensity per unit GDP, further shift the industrial structure, and transfer to a low carbon economy and society are the feasible pathways. As the largest energy consumer and GHG emitter, power sector plays a key role in guaranteeing China's energy security and achieving environmental sustainability. In 2007, the State Council issued *Energy-saving Generation Dispatch Regulation*, which aims to improve energy and environmental issues in power sector through shifting the dispatch mode.

Many researches have been conducting energy-saving and economic generation dispatch issues. Zhu, Song et al. (2011) made a qualitative analysis on the influencing factors of energy-saving generation dispatch and put forward some recommendations on modifying the dispatch mode. Shen, Liu (2011) established optimization models to explore the optimal unit commitment for energy-saving generation dispatch. Li, Shi (2010) emphasizes the influence of wind power to grid stability and established economic generation dispatch model based on modified positive rotation constraint. Wang, Qiao (2012) studied on the compensation mechanism on energy-saving generation dispatch, including generation permits trade, government compensation and compensation based on capacity etc.

This paper will establish an optimization model for energy-saving generation dispatch with a consideration of CO₂ emission limitation and the development of new energy materials which promotes the development of solar energy, wind energy and biomass energy.

2. energy-saving generation dispatch based on the development of new energy materials

2.1 objective function

Economic generation dispatch is to find out the optimal unit commitment which not only satisfies the power demand but also guarantees the grid security. The load of power can be divided into three basic zones, which are base load, shoulder load and peak load. Base load means load below the minimum load level, shoulder load means load between the minimum load level and the average load level, and peak load means load above the average load level. One key objective of economic generation dispatch is to achieve the least generation cost at the whole power supply system level. So the objective function can be described as Eq. (1)

$$(P) \text{ Min } \sum_{i=1}^I \{ [\sigma_{bi} (a_i + b_i P_{bi} + c_i P_{bi}^2)] + [\sigma_{si} (a_i + b_i P_{si} + c_i P_{si}^2)] + [\sigma_{pi} (a_i + b_i P_{pi} + c_i P_{pi}^2)] \} \quad (1)$$

where, P_{bi} represents the real power of unit i during the base load period; P_{si} represents the real power of unit i during the shoulder load period; P_{pi} represents the real power of unit i during the peak load period; $a_i + b_i P_i + c_i P_i^2$ represents coal consumption of unit i .

2.2 model constraints

2.2.1 real power for base load demand

The power generation of unit i for base load can be mathematically described as the follows.

$$\sum_{i=1}^I \sigma_{bi} P_{bi} = \text{load}_b (1 + \text{loss}_b) \quad (2)$$

where, loss_b represents the percentage of power loss during base load period;

2.2.2 power generation for base load demand

The power generation of unit i to satisfy the base load demand is described as the follows,

$$q_{bi} = P_{bi} * T_b * (1 - \lambda_i) \quad (3)$$

where, q_{bi} represents the power generation of unit i during base load period; λ_i represents unavailability of unit i ; T_b represents the duration period of base load.

2.2.3 power demand of base load period

$$\sum_{i=1}^I \sigma_{bi} q_{bi} * (1 - \beta_i) = Q_b \quad (4)$$

where, Q_b represents the power demand of the base load period; β_i represents the auxiliary power ratio;

2.2.4 real power for shoulder load demand

$$\sum_{i=1}^I \sigma_{si} P_{si} = (\text{load}_s - \text{load}_b) (1 + \text{loss}_s) \quad (5)$$

2.2.5 power generation for shoulder load demand

$$q_{si} = P_{si} * T_s (1 - \lambda_i) \quad (6)$$

where, q_{si} represents the power generation of unit i during base load period; T_s represents the duration period of base load.

2.2.6 power demand of shoulder load period

$$\sum_{i=1}^I \sigma_{si} q_{si} * (1 - \beta_i) = Q_s \quad (7)$$

where, Q_s represents the power demand during shoulder load period.

2.2.7 real power for peak load demand

$$\sum_{i=1}^I \sigma_{pi} P_{pi} = (load_p - load_s) (1 + loss_p) \quad (8)$$

where, P_{pi} represents the real power of unit i during peak load period.

2.2.8 power generation for peak load demand

$$q_{pi} = P_{pi} * T_p (1 - \lambda_i) \quad (9)$$

where, q_{pi} represents the power generation of unit i during peak load period; T_p represents the duration of peak load period.

2.2.9 power demand of peak load period

$$\sum_{i=1}^I q_{pi} * (1 - \beta_i) = Q_p \quad (10)$$

where, Q_p represents the power demand during peak load period.

2.2.10 power reserve for peak load demand

$$\sum_{i=1}^I \sigma_{ri} P_{ri} = load_p * load_r \quad (11)$$

where, P_{ri} represents power generation for reservation of unit i ; $load_r$ represents the ratio between power generation for reservation and the peak load demand.

2.2.11 real power of unit i

The real power of unit i should be the sum of its real power during each load period and that for reservation.

$$P_i = \sigma_{bi} P_{bi} + \sigma_{si} P_{si} + \sigma_{pi} P_{pi} + \sigma_{ri} P_{ri} \quad (12)$$

2.2.12 contract performance

During the process of economic generation dispatch, each unit has the obligation to execute the contract. Therefore, the amount of power generated by unit i during the should not be less than the contractual amount.

$$(q_{bi} + q_{si} + q_{pi}) (1 - \beta_i) \geq q_{ci} \quad (13)$$

where, q_{ci} represents the contractual power generation quantity.

2.2.12 coal consumption

$$coal_i = \eta_{bi} q_{bi} + \eta_{si} q_{si} + \eta_{pi} q_{pi} \quad (14)$$

where, $coal_i$ represents coal consumption of unit i ; η_{bi} represents the coal consumption of unit i for base load demand generation; η_{si} represents the coal consumption of unit i for shoulder load demand generation; η_{pi} represents the coal consumption of unit i for peak load demand generation.

2.2.13 CO₂ emission limit

$$co_{2i} = \omega * coal_i \quad (15)$$

where, ω represents the coefficient of CO₂ emission of unit i .

3. Conclusion

The development of new energy materials has dramatically promoted the expansion of renewable and other clean energy, such as wind, solar, biomass, geothermal and nuclear energy. How to guarantee all the above clean power get connected to the grid requires more advanced economic and energy-saving generation dispatch.

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Tribological behavior of ball-milled expanded graphite/B powders in a high-energy mill

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Key words: Graphite; Metal nanoparticles; Anti-friction; Wear

Abstract. A mixture of expanded graphite (EG) and boron was ball-milled in a high-energy mill. The microstructure of the milled EG/B powders was characterized by transmission electron microscopy (TEM). The tribological behavior of the milled powders used as lubricating additive was investigated by using a tribo-tester, and the morphology of the worn tribo-surfaces were observed by scanning electron microscope (SEM). The results show that the powders used as lubricating additive have an obvious anti-friction and wear resistance effect, and the larger the applied load, the lower the friction coefficient and the wear severity.

Introduction

Graphite has been widely used as solid lubricants due to its unique properties, such as self-lubricating, high temperature resistance, and corrosion resistance [1, 2]. Recently, Huang et al. [3] reported that graphite nanosheets used as additive produced by ball-milling natural graphite could effectively improve the anti-friction ability of base oil. In addition, reports [4-6] proved that some metal nanoparticles used as lubricating additive had an excellent anti-friction effect and self-repair effect for the friction surface. It is deduced that a mixture of graphite nanosheets and metal nanoparticles used as additive may combine the self-lubricating effect of graphite and self-repair effect of metal nanoparticles. Expanded graphite (EG) is a new carbon material with a highly porous structure. Compared with natural graphite, the violently expanded graphite flakes of EG may be helpful for the contact between the graphite flakes and metal powders during ball milling. In the present work, a mixture of EG and boron powders were ball milled. We attempted to investigate anti-friction and wear effect of the milled EG/B powders used as lubricating additive.

Experimental

At room temperature, 10 mL of concentrated sulphuric acid (98%) and 1 mL of hydrogen peroxide (30%) were mixed with 6 g of natural flake graphite (35 mesh, 99% purity, 97.5% crystallinity, purchased from Qingdao Tianhe Graphite Company, China). The mixture was placed for 90 min, washed with water to pH 5-7 and dried at 80 °C for 24 h, forming expandable graphite. The expandable graphite was rapidly heated at 600 °C for 15-25 s, forming EG.

EG was mixed with boron powders (200 mesh, 99.9% purity) in 5:1 weight ratio, forming EG/B mixture. With a ball-to-mixture weight ratio of 40:1, 2 g of the EG-B mixture and 80 g of GCr15 (52100) bearing steel balls were introduced to a steel vial. For preventing the agglomeration of the powders, 180 mL of ethanol as a milling medium was poured into the vial. The powders were ball-milled for 80 h in a GN-2 high-energy planetary-type mill (Shenyang New Electromechanical Equipment Factory, China) under an air atmosphere with a rotation speed of 450 rpm. The microstructure of the milled powders was characterized by transmission electron microscopy (TEM, JEOL-2010).

The tribological test of the milled EG/B powders was carried out on a MMU-5G tribo- tester at room temperature. GCr15 steel was used as the upper specimen with an inside diameter of 20 mm and an outside diameter of 26 mm, and 45# carbon steel was used as the mating lower specimen with a radius of 50 mm. Lubricant was prepared by adding the milled EG-B mixtures into a fully

formulated mineral gasoline engine oil SJ/5W-40. Prior to each tribotest run, the lubricant was ultrasonically treated for 5 minutes to keep an uniform dispersion of the powders in the base oil, and then about 40 μL of lubricant was supplied onto the contact area. The morphologies of the worn tribo-surfaces were observed under scanning electron microscope (SEM, KY2500).

Results and discussion

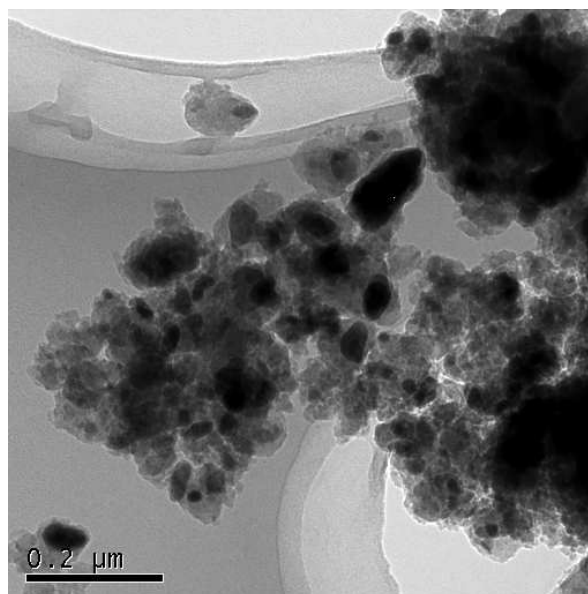


Fig.1 TEM image of milled EG/B powders

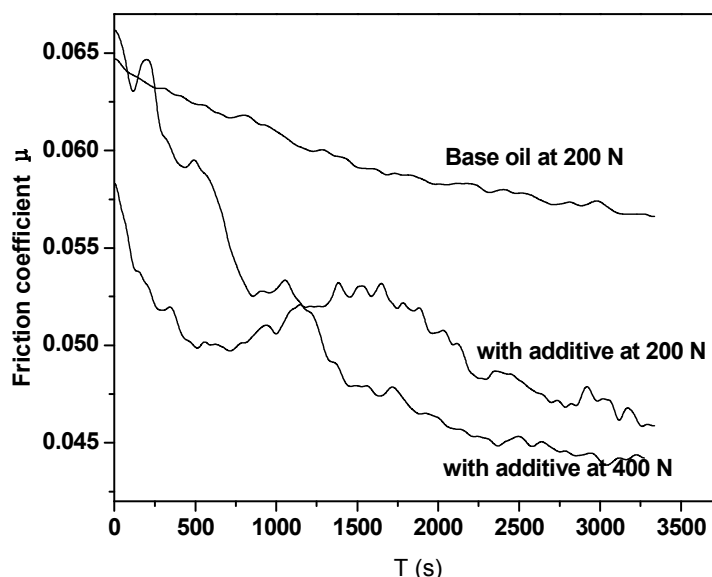


Fig.2 Friction coefficient of lubricants with milled EG/B powders at different applied loads.

Fig.1 shows the TEM image of the ball-milled EG/B powders, where boron particles with a size of several to several tens nanometers are dispersed in graphite aggregates.

Fig.2 presents the friction coefficient evolution for base oil and base oil with the milled EG/B powders with running duration. It is seen that under the same applied loads, 200 N, the friction coefficient of the base oil is higher than that of the lubricant with the powders. When the applied load increases to 400 N, the friction coefficient further decreases. In addition, the friction coefficient of the above three lubricants all exhibits a downtrend. Compared with base oil, the downtrend of the two lubricants with the powders is sharper.

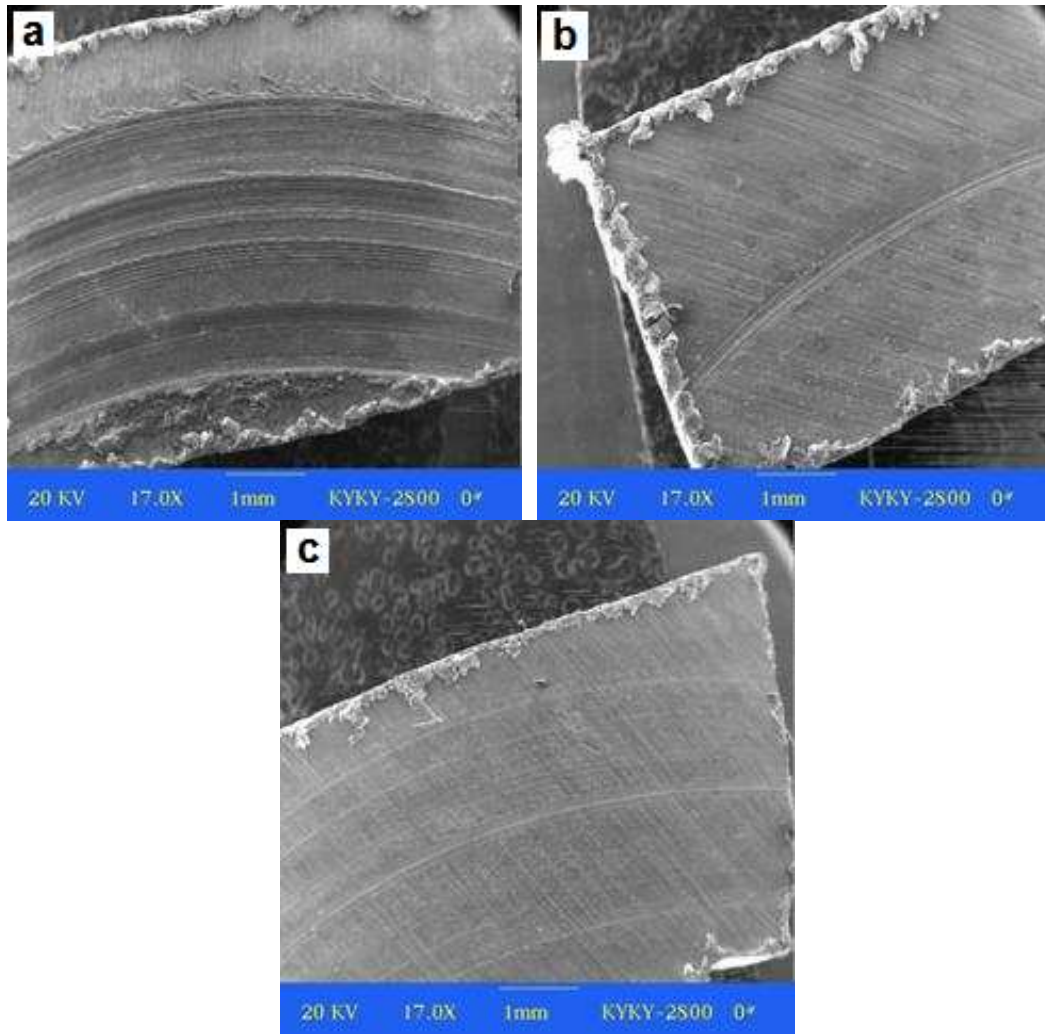


Fig .3 SEM images of worn lower specimen surfaces for base oil at 200 N (a), lubricant with milled EG/B powders at 200 N(b) and 400 N (c)

Fig.3 shows the representative morphologies of the worn surfaces for the lower 45# carbon steel specimens under different conditions. The wear modes for the three specimens mainly belong to a grain abrasion. The wear severity, however, varies depending on the applied conditions. For base oil at 200 N, the ploughing grooves on the worn surfaces are the deepest and widest, and the friction degree is the most serious. For the lubricant with the milled EG/B powders at 200 N, the ploughing grooves become slenderer and shallower, and the friction degree is reduced. Increasing the applied load to 400 N, the ploughing grooves are the most slender and shallow, and the friction degree is the slightest.

The results show that the the milled EG/B powders used as lubricating additive has an obvious anti-friction and wear resistance effect, and the lager the applied load, the lower the friction coefficient and the wear severity.

4. Conclusion

By ball milling a mixture of EG and boron powders, we obtain a compound comprising boron nanoparticles dispersed in graphite aggregates. The milled EG/B powders used as lubricating additive show an obvious anti-friction and wear resistance effect, and the lager the applied load, the lower the friction coefficient and the wear severity.

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CHAPTER 2:

Chemical Engineering

Preparation and Properties of Magnesium Based Hydrogen Storage Alloy Mg_2NiH_4 in Chemical Engineering

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Keywords: Magnesium based hydrogen storage alloy; preparation; Ammonium Perchlorate; thermal decomposition; catalysis

Abstract. Mg_2NiH_4 was prepared by replacement-diffusion method, and its structure was determined by XRD, ICP and DSC-TG. The influence of Mg_2NiH_4 on the thermal decomposition behaviour for ammonium perchlorate (AP) was carried out by thermal analysis (DSC). Results show that Mg_2NiH_4 has obvious catalytic effect on the thermal decomposition of AP. This catalytic effect of Mg_2NiH_4 was enhanced with its increase in content, and the DSC heat release for AP was on its biggest value when the content of Mg_2NiH_4 was 30%. With the increase of hydrogen storage, the catalytic effect of Mg-Ni hydrogen storage alloys became stronger.

Introduction

Magnesium-based alloy are amongst the most attractive materials for hydrogen storage, since hydrogen capacity exceeds all known reversible metal hydrides [1,2]. However, almost no practical application remains because of its poor hydriding–dehydriding properties at ambient temperature: thermodynamically too stable and kinetically too slow by far. Mg_2NiH_4 is one of the magnesium based hydrogen storage material, and it provides nominally 3.6 wt.% of hydrogen and large enthalpy of hydride formation [3]. These features suggest it as an energetic component for rocket propellants.

Ammonium perchlorate (AP) is used as the most common oxidizer in solid rocket propellant and its nature is believed to influence the performance of the solid rocket propellant [4, 5]. In this paper, Mg_2NiH_4 was prepared and its effect on the thermal decomposition of AP was also studied by thermal analysis (DSC).

Experimental

Preparation of Mg_2NiH_4 . Mg_2Ni was prepared by the replacement-diffusion method (RDM) according to published methods [3,6]. Mg_2NiH_4 was directly prepared from the reaction of Mg_2Ni with hydrogen. Mg_2Ni was reacted with 6 MPa hydrogen at 350°C for 4 h in a stainless steel reactor and finally Mg_2NiH_4 was obtained.

The sample was characterized by X-ray diffraction (XRD) using on a Bruker D8 Siemens diffractometer with Cu K α radiation. The Mg and Ni content were determined by ICP—OES (Perkin Elmer Optima 2000 DV). The hydrogen concentration and dehydriding properties Mg_2NiH_4 were examined by a thermogravimetry (TG) and differential thermalanalysis (DSC) (TA DSC-TG SDT Q600) equipment under an atmosphere of N_2 (at a rate of 20ml/min) and at a heating rate of 20°C. min⁻¹.

DSC studies. To prepare the samples for the thermal decomposition experiments, Mg_2NiH_4 and AP were mixed and ground for ten minutes, and then used for DSC-TG studies. DSC studies were performed with the thermal analyzer TA DSC-TG SDT Q600 apparatus under an atmosphere of N_2 (at a rate 20ml/min) at a heating rate of 20°C min⁻¹.

Results and discussion

XRD patterns. Fig.1 is the XRD spectrum of Mg_2Ni and Mg_2NiH_4 . Mg_2Ni has a hexagonal crystal structure and hydride has a monoclinic crystal structure which is completely different from that of Mg_2Ni . There is no obvious oxide phase and Mg phase trace.

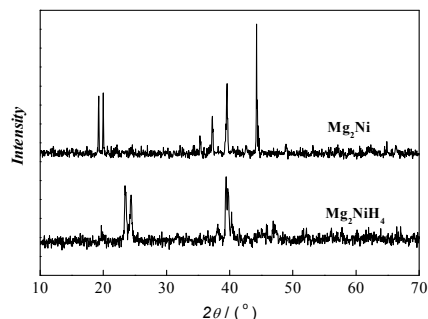


Fig 1. XRD pattern of Mg-based hydrogen storage alloy Mg_2NiH_4

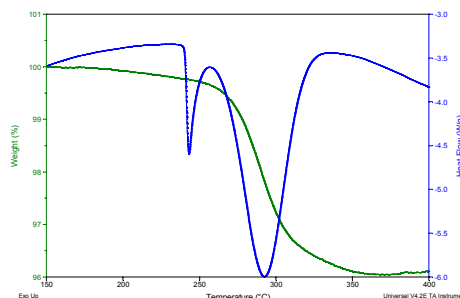


Fig 2. DSC-TG curve of Mg_2NiH_4

ICP analysis indicated that the Mg and Ni content in Mg_2Ni were 46.5 wt% and 53.4 wt% respectively. The Mg and Ni content in Mg_2NiH_4 were 44.3wt% and 52.6wt%. They are also close to their theoretical value.

Fig.2 is the DSC-TG curve of the Mg_2NiH_4 . The DSC curve for the decomposition of Mg_2NiH_4 shows two events. The endothermic DSC peak at 245 °C represents the transition from low temperature form (LT) to high temperature form (HT). The endothermic DSC peak at 280 °C represents the dehydrogenation reaction. The dehydrogenation reaction is: $\text{Mg}_2\text{NiH}_4 = \text{Mg}_2\text{Ni} + 2\text{H}_2$. It can also be seen from the thermogravimetry (TG) profile that the hydrogen content of Mg_2NiH_4 is about 3.6%.

Effects of Mg_2NiH_4 on the thermal decomposition of AP. The DSC curve for the decomposition of pure AP shows three events [7,8]. The endothermic DSC peak at 249 °C represents the transition from orthorhombic form to cubic form. The thermal decomposition of AP occurs in two steps. The first exothermic peak at low temperature 322.7 °C corresponds to the partial decomposition of AP and formation of an intermediate. The second, main exothermic peak at higher temperature 477.2 °C corresponds to the complete decomposition of the intermediate to volatile products.

The DSC curves for the decomposition of AP in the presence of Mg_2NiH_4 show a noticeable change in the decomposition pattern (Fig.3). The endothermic peak shows no changes in position. In contrast, there were noticeable changes to the first and second exothermic peak. Their position depended strongly on Mg_2NiH_4 . The addition of Mg_2NiH_4 (5wt%) lower the second exothermic peak temperature of AP by 88.9 °C, while increase the first exothermic peak temperature of AP by 18.7 °C. This indicates that Mg_2NiH_4 show obvious catalytic effect on the main exothermic decomposition of

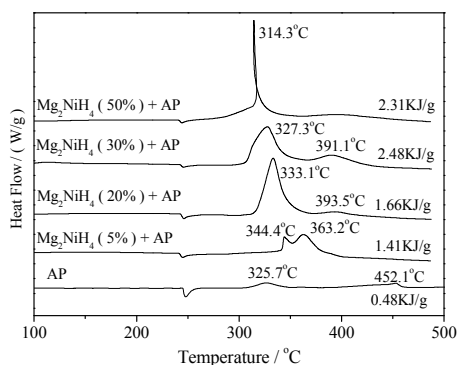


Fig 3. DSC curves of the mixtures of AP and Mg_2NiH_4

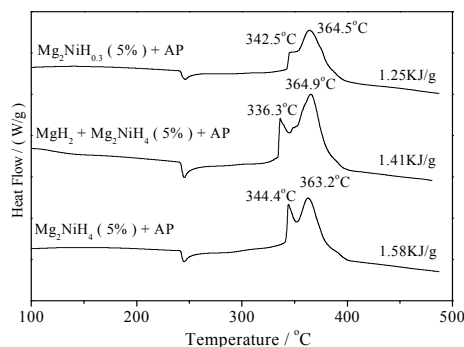


Fig 4. DSC curves of the mixtures of AP and hydrogen storage alloys with different component

AP and hindering effect on the first exothermic decomposition of AP. The total DSC heat release of AP in the presence of Mg_2NiH_4 (5wt%) was increased from 0.48 kJ/g to 1.41 kJ/g, showing that Mg_2NiH_4 clearly promoted the decomposition of AP.

Effects of Mg_2NiH_4 with different contents on the thermal decomposition of AP.

As shown in Fig. 3, with the increase of the content of Mg_2NiH_4 , the first and second exothermic peak temperature of AP went down and the total DSC heat release went up. It indicates that the catalytic effect of Mg_2NiH_4 on the first and second decomposition of AP become stronger with the increase of Mg_2NiH_4 content. When the content of Mg_2NiH_4 was more than 20wt%, the first exothermic peak of AP was obviously bigger than the second exothermic peak, showing that the catalytic effect of Mg_2NiH_4 on the first decomposition of AP is apparently stronger than that of the second decomposition. This result show that the decomposition process of AP is changed thoroughly and the main decomposition step of AP is on the first decomposition step. It can be seen that when the content of Mg_2NiH_4 was 50%, the first exothermic peak of AP become very high and narrow. This result is due to the quick and violent decomposition of AP at the first exothermic peak temperature. However, when the addition of Mg_2NiH_4 was 50%, the total DSC heat release of AP was less than that of 30%.

Effects of Mg-Ni hydrogen storage alloys with different hydrogen content on the thermal decomposition of AP. It can be seen from Fig. 4 that magnesium based hydrogen storage alloys with different hydrogen content all decreased the second exothermic peak temperature of AP, while increase the first exothermic peak temperature of AP, showing good catalyzed effect on the second exothermic decomposition and hindering effect on the first exothermic decomposition of AP. We also could find from Fig. 4 and table 2 that the first or second exothermic peak temperature of the mixture of AP and hydrogen storage alloys with different hydrogen content was approximative, while the total DSC heat release went up with the increase of hydrogen content. It is clear that the promoting effect become stronger with the increase of hydrogen content.

Conclusion

This study reveals that Mg_2NiH_4 has good catalytic and intensifying effect on the thermal decomposition of AP and it becomes stronger with the content of Mg_2NiH_4 increase. The effect of Mg-Ni hydrogen storage alloys on the total DSC heat release of AP is associated with the content of hydrogen. Due to the obvious intensifying effect on the decomposition of AP, Mg-Ni hydrogen storage alloys will improve the combustion performance of the solid rocket propellant including AP.

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Effect of Stabilizer and Molding Technics in Chemical Engineering on the Stabilization of Sulfate Rich Soil

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Keywords: sulfate rich soil; stabilization; stabilizer; molding technics.

Abstract. In chemical engineering field, ettringite (AFt) formation effect the stabilization of sulfate rich soil mixed with cementitious materials. The different stabilizer compositions and twice molding technics may avoid and repair the destruction caused by AFt with decreasing the production rate of calcium silicate hydrates(C-S-H) and eliminating the void in stabilized soils. The results show that the strength of stabilized 5% sodium sulfate bearing soils, under above methods, are not less than that of the control ones, and the specimens keep steady after soaking in 5% sodium sulfate solution for 12 weeks.

Introduction

There are $3.7 \times 10^5 \text{ km}^2$ saline soils in China, in which high and ultra-sulfate based soil account for great proportion of the soils(salt content is 5 percent or higher)[1,2]. Sulfate based soil bases need to be treated to meet the highway construction requirements. Stabilizer is an important technical method in saline soil bases treatment [3]. The use of calcium-based additives (lime, cement, and Class C fly ash) to treat soils and bases has been performed with success over many years. Over the past 20 years, a phenomenon has surfaced in which many subgrade soils treated with calcium-based stabilizers experience heaving problems as being due to the formation of ettringite, an expansion mineral which is a reaction product formed by the chemical reactions with sulfate and/or sulfide minerals and calcium-modified soils [4]. Therefore, calcium-based stabilizers cannot meet the engineering stabilization requirement of sulfate rich soil.

Texas Transportation Institute, Texas Department of Transportation and Texas A&M University [5], etc. use sulfate-resistant cement, ground granulated blast furnace slag (GGBS) and fly ash substitute cement or lime to stabilize sulfate bearing soils, which can stabilize sulfate bearing soils effectively with decreasing the active calcium and aluminum content in stabilizer, but the method does not solve the stabilization of high sulfate based soil satisfactorily.

Experimental

There are two reactions in the stabilization of sulfate bearing soil: C-S-H consolidates soil particles and forms the structure of stabilized soil, and AFt expands, which destroys the structure and forms new cracks. According to the two reactions, the stabilization of sulfate bearing soil need take measures in stabilization mix and stabilization technics. Decreasing the formation rate of C-S-H with adjusting stabilizer mix, which can prevent the destroy of C-S-H caused by AFt expansion when they form in the same time; after the AFt expansion ends, the stabilized soil need be compacted again, which can eliminate the crack caused by AFt formation. In mix, the active calcium content need be control to meet the formation of cementitious hydrates, like C-S-H and avoid more calcium to form AFt with aluminum and sulfate produced in the saline soil. Based on the technical measures, the whole test plan is given in Table 1.

(1)Soil: control soil is Beijing nature soil, and the physical properties are given in Table 2; artificial sulfate soil: Beijing soil+5% sulfate sodium (dry soil mass ratio).

(2)Stabilizer: P.O.32.5 and GGBS, come from Hebei Jidong Cement Plant and Shougang Co.Ltd., were used, Calcium Hydroxide (AR) is supplied by Beijing Beihua Fine Chemical Co., Ltd., Beijing, China.The chemical properties of GGBS are presented in Table 3.

(3)Stabilized soils were made by mixing the soils with stabilizer according to mix composition by the SJ-160 Mixer. The specific process was as follow:

a)Dry Soil was added into the container, mixing 60 seconds with slow speed (60 r/min);b)Stabilizer were put in container, mixing 30 seconds with slow speed (60 r/min); c)Intermittent hand mixing with palette knife to achieve a homogeneous mixture, and then the admixture was mixed 120 seconds with high speed (140r/min);d) Mixed admixture was filled in cube steel mould (5cm×5cm×5cm), and was compacted.

(4)Mold Technics: a) Control soils are remolded after 24h (A); saline soil specimens are remolded with two methods. One is normal remolded after 24h, the other is first remolded after 24h and then is compacted after the specimen's expansion is end (B, twice compaction).

(5)Strength and durability test: The strength of NO.1-3 were tested on 1, 3, 7, 28d to examine the effect of GGBS substitutes P.O. on the formation rate of C-S-H and the strength of stabilized soil; NO.4-6, as control specimens, were cured 28 days in standard condition ($20^{\circ}\text{C} \pm 2^{\circ}\text{C}$, $\text{RH} \geq 95\%$) and were soaked in deioned water; NO.7-12 were cured 28 days in standard condition and were soaked 5% sodium sulfate solution; the strength of NO.4-12 were tested on different soaking time (4w, 8w and 12w). Strength test is according to JTJ051-93. The durability assesses focus on the difference of the strength of stabilized soils in difference soaking time in 5% Na_2SO_4 .

Table 1 Testing plan of stabilization and different age strengths of specimens of stabilized saline soil

(a) Testing program and strengths of stabilized soil(NO.1-3)

NO.	Soil	Molding Technics	Mix P.O.-GGBS-CH	Strength/MPa			
				1d	3d	7d	28d
1	Control Soil	A	10-0-0	1.63	1.85	2.26	5.11
2		A	4-5-1	0.83	1.47	2.16	6.49
3		A	2-8-0	0.58	1.24	2.05	6.58

(b) Testing program and strengths of stabilized soil(NO.4-12)

NO	Soil	Molding Technics	Soaking solution	Mix P.O.-GGBS-CH	The strength in different soaking time after 28d in standard condition /MPa		
					4w	8w	12w
4	Control Soil	A	Deioned water	4-5-1	11.58	11.64	12.05
5				2-8-0	11.61	11.73	11.92
6				0-8.3-1.7	9.97	11.56	12.76
7	Sulfate Based Soil	A	5% Sulfate Sodium Solution	4-5-1	4.26	4.54	4.56
8		A		2-8-0	6.02	6.12	7.56
9		A		0-8.3-1.7	6.22	6.19	9.07
10		B		4-5-1	6.69	7.57	7.34
11		B		2-8-0	NT	12.18	NT
12		B		0-8.3-1.7	NT	12.03	NT

PS: NT means the test is not performed.

Table 2 Physical properties of Beijing soil

Soil	ρ (g/cm^3)	G_s	W (%)	I_L	I_p
Beijing Soil	2.06	2.71	21.08	0.29	11.50

Table 3 Chemical compositions of GGBS

Composition/ %	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃
GGBS	36.5	7.5	0.3	38.5	6.0	0.01

Results and Discussion

Table 1(a) shows the initial strengths of NO.1-3, with the increment of GGBS content in the stabilizer, decrease accordingly, especially for the strength of 1d; but the final strengths of specimens with GGBS (28d) are higher than the specimen without GGBS, which shows the initial formation rate of hydrates, like C-S-H, become lower, vice versa.

On the condition of enough calcium, active aluminum and sulfate exist in soil, AFt forms fast in early stabilized soil [6], the test results of Table 1 show GGBS can decrease the formation rate and content of C-S-H in early stabilized soil. NO.7 is with 50% cement content in the stabilizer, which cause the formation rate of early C-S-H becomes fast, the early content is major in the whole content, so the fast formation of AFt destroys the cementitious structure formed by C-S-H, when AFt forms steadily, the content of according C-S-H is little, the property of restoring and building the structure of stabilized soil, and the content of pore produced by AFt expansion is relative more because the early structure of stabilized soil is dense and stiffness of stabilized soil is big, which cause the strength loss of NO.7 is higher with compare to NO.8 and NO.9.

In the specimens of NO.8 and 9, the content of GGBS is relative higher the stabilized soil, which means the early formation content of C-S-H is relative lower and the structure of stabilized soil is relative elastic, and can tolerate the formation of AFt, which does not destroy the structure severely. After the formation of AFt become steadily, the later formation of C-S-H is relative more, so the strength of stabilized soil is relative high. The results show the influence of the expansion of AFt on the stabilized soil can be diminish with adjusting the stabilizer mix and the relative formation rate of AFt and C-S-H in stabilized soil.

Table 1(b) shows twice compaction can increase the strength of stabilized soil obviously. The specimens are different in strength with the same mix and different mold technics, like the specimen of NO. 4,7 and 10. The 24 hours remolding, because the main formation progress of AFt is restrained in mould, the expansion does not produce more cracks, though the formation of AFt, after remolding, would produce new cracks and ruin the structure, the destroy produce relative less cracks, as to the specimens with twice compaction measure, the cracks formed by AFt can be mostly diminished by the measure and the C-S-H formed in later period can cement the soil more efficiency, therefore the strength loss is lower.

The effects of twice compaction on the stabilized soil, for different mixes, are different in Table 1(b). In the different mixes, twice compaction caused the different strength increment. For the mix of 4-5-1(P.O.-GGBS-CH), because the C-S-H formed fast, the C-S-H were destroyed by AFt expansion, even with twice compaction measure, the strength loss of stabilized soil were still more. As to the mixes of 2-8-0 and 0-8.3-1.7, the early formation rate of C-S-H was lower, and the C-S-H destroyed was little. After twice compaction, the C-S-H still largely form and cement soil particles to produce dense structure, meanwhile offsetting the negative effects of AFt expansion.

In a word, the test results indicate sulfate rich soil (5% Na₂SO₄) can be stabilized with adjusting stabilizer mix and taking twice compaction measure, the strength of stabilized soil can keep steadily, after soaking in 5% Na₂SO₄ for 12 weeks.

Conclusion

(1) Because AFt mainly form in early period, cement is partly and completely substituted by GGBS, the formation rate and content of C-S-H will be decreased and avoid the destroy caused by AFt, meanwhile, the main C-S-H forms in lately period, which is good for the structure formation of stabilized soil.

(2)The specimens with twice compaction can delete the early cracks produced by AFt formation and expansion, and increase the strengths of stabilized soils.

(3)Adjusting stabilizer mixes and twice compaction can most efficiency decrease the negative effect caused by AFt expansion, and keep more C-S-H forming after the AFt expansion in the stabilized soil.

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Determination of β -sitosterol with Chemical Course and Material Applications in Jatropha Seed Oil by High Performance Liquid Chromatography

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Keywords: Jatropha, sitosterol, Chromatography

Abstract. A simple and rapid high performance liquid chromatography (HPLC) assay was developed to identify and measure the β -sitosterol with chemical course and material applications in jatropha seed oil. The stigmaterol was isolated with a good selectivity by HPLC employing reversed phase C18 columns. The components were separated by mobile phase of methanol-water (99/1, v/v) and detected at 205nm. The quantitation of the stigmaterol was reproducible and the method relative standard deviation is 1.1%. The mean analytical recovery was 96.2%.

Introduction

Jatropha curcas L. (Euphorbiaceae) is an oil-bearing shrub widely distributed in many Latin American, Asian, and African countries. The seed kernels, which contain up to 60% oil with a fatty acid composition similar to that of common edible oils^{3,4} are the most interesting parts of the plant from a potential commercial vantage point^[1]. It was founded that plants with higher fat content usually also contain more phytosterols. β -sitosterol is one of the major component of phytosterol. β -sitosterol induces apoptosis in breast cancer cells, on two pathways leading to apoptosis ^[2]. In this paper, a simple and rapid high performance liquid chromatography (HPLC) Assay was developed to identify and measure β -sitosterol with chemical course and material applications in jatropha seed oil.

Material and methods

Reagents and chemicals. Dehydrated alcohol was purchased from the Nan Jing Jian Chen Biotechnology Lt. Cod (NanJing, China). Two reagents used were of analytical grade. Methanol (HPLC Grade) was purchased from Romil Ltd. (The Source, Waterbeach, Cambridge, UK). β -sitosterol were purchased from Sigma (St. Louis, MO, USA). Water was obtained from a Milli-Q system (Millipore, Bedford, MA, USA) and all samples were filtered using durapore (PVDF) filters purchased from the same source. Jatropha seeds were purchased from Guizhou province of China. The sample was ground in a blender to produce a fine powder.

Instrumentation and chromatographic conditions. All experiments were performed using a Agilent 1200 HPLC system equipped with a separation module, a DAD detector (model 2996), an online degasser, an autosampler and a Waters C18 Column (5 μ m, 250mm $\times$ 4.6mm i.d.). The chromatographic elution was accomplished isocratically with methanol–water (99:1 v/v) at a flow rate of 1 ml/min. The temperature was maintained at a room temperature and the injection volume was 20 μ L. DAD detection was achieved in the range of 200–800 nm, 205nm results were used for quantitative purposes.

Preparation of standard solutions. Separate stock solutions of the reference standards were made by weighing out appropriate amounts into volumetric flasks and filling to volume with methanol. Serial dilutions of the relevant stock solutions were made to prepare five concentrations of each standard solution over the concentration range of 0.01-0.06 mg/ml. These solutions were used for the linearity experiments. The concentration (0.04mg/ml) of the standard solutions was separately

prepared for use in the accuracy experiments. The solutions with low, medium and high concentrations (0.02mg/ml, 0.04mg/ml, 0.06mg/ml) were separately prepared for use in the recovery experiments.

Sample preparation and extraction. Ten gram, Jatropha seeds powder was placed in six 250 ml round bottom flasks. Then 80 ml solvent of acetidin was added into the flasks. The extracts were in the flasks in a heated water bath shaker for extraction (60°C, 1 h) and vacuum filtered to remove solvents. Combined filtrate was vacuum evaporated to recover the solvent at 25°C. Evaporation of the organic solvent under reduced pressure gave the jatropha seeds oil. Jatropha seeds oil (10mg) was weighed into a 10ml volumetric flask and 10ml of dehydrated alcohol was added. The solution was filtered through a 0.45µm PVDF membrane and analyzed.

Result and discussion

Method development. As shown in Fig.1, the β -sitosterol was well separated within 12 min using isocratic elution with methanol: water (99:1 v/v) at a room temperature and a flow rate of 1 ml/min. The retention time was 10.782 min. As shown in Fig.2, an increase in methanol content in the mobile phase reduced the resolution of β -sitosterol. As shown in Fig.3, substitution of the mobile phase with acetonitrile : water (99:1 v/v) reduced the resolution of β -sitosterol. As shown in Table.1, maximum absorption differed with different wavelength and was in turn 254.9 at 205nm, 130.9 at 210nm, 46 at 215nm, 19 at 220nm. Result indicated that maximum absorption was achieved at 205nm. Therefore, 205nm was used as the determination wavelength in the experiment.

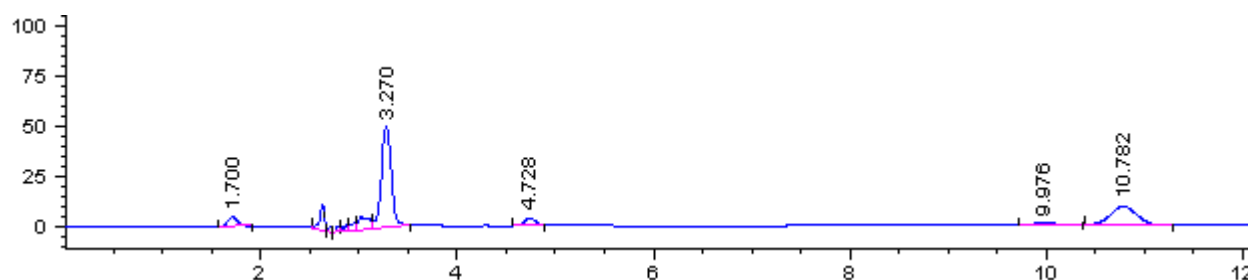


Fig. 1 UV chromatograms of β -sitosterol standard solution with methanol: water (99:1 v/v)

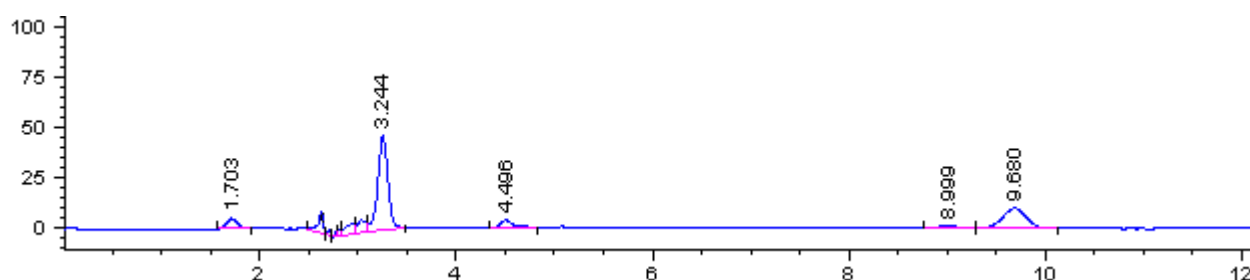


Fig. 2 UV chromatograms of β -sitosterol standard solution with methanol

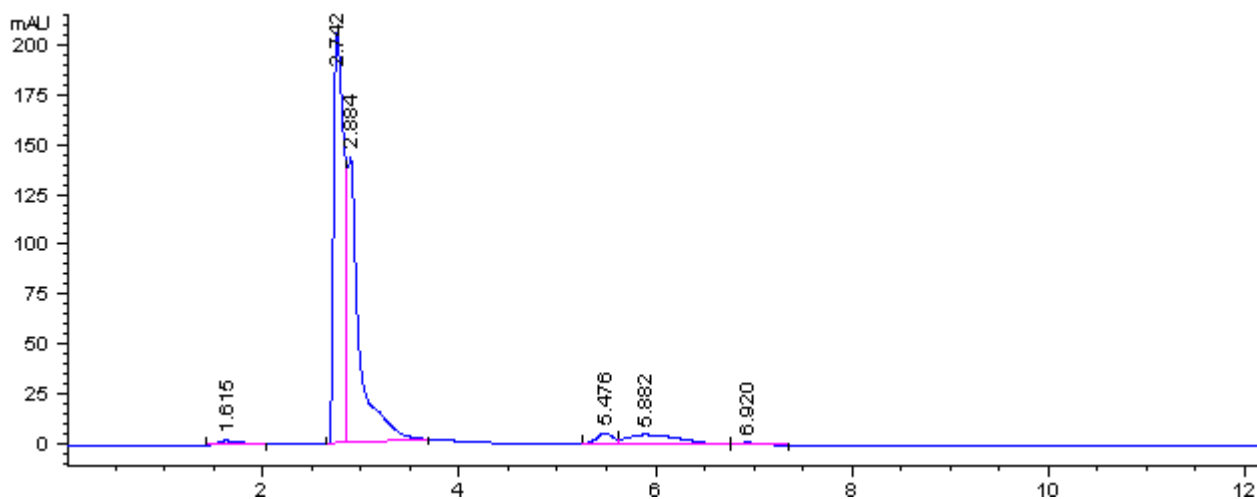


Fig. 3 UV chromatograms of β -sitosterol standard solution with acetonitrile : water (99:1 v/v)

Table 1 Peak area of β -sitosterol at different wavelength

Wavelength (nm)	Peak area
205	254.9
210	130.9
215	46
220	19

Linearity. As shown in Fig. 4, six concentrations of each standard solution were processed for linearity. The UV mode resulted in a determination coefficient of $R^2=0.998$ at a concentration range of 0.01–0.06 mg/ml. The linear equation was $y=13091x-16.485$.

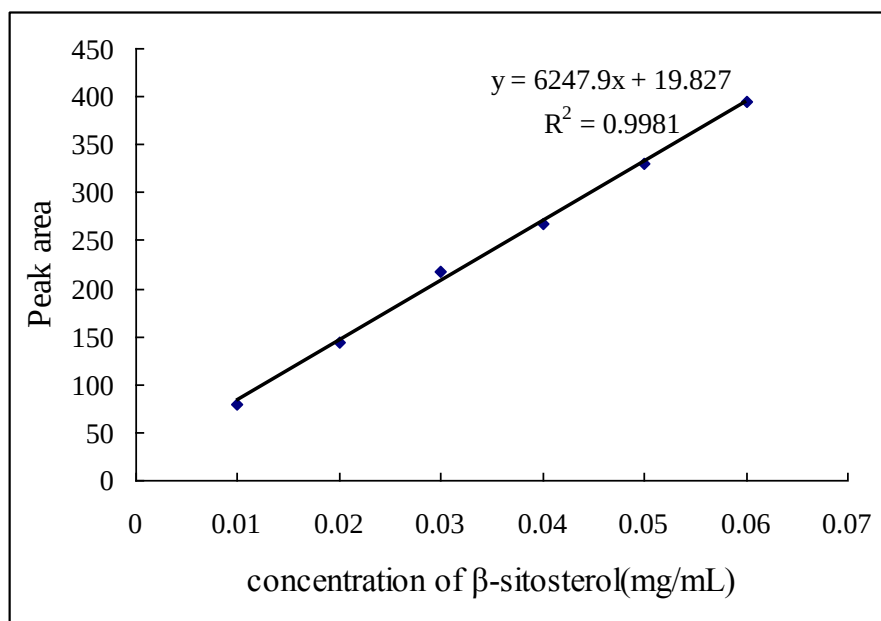


Fig.4 Standard curve of β -sitosterol

Precision. The precision of the method were determined by analysing the concentration (0.03mg/ml) of the standard solutions five times, which was prepared as described earlier in the section of preparation of standard solutions. The percentage precision was calculated using the relative standard deviation and was found to be 1.1% (Table 2).

Table 2 Precision of β -sitosterol

Concentration (mg/ml)	Peak Area					RSD (%)
	1	2	3	4	5	
0.04	169.5	171.5	169.3	167.7	171.8	1.1

Recovery. The solutions with low, medium and high concentrations (0.02mg/ml, 0.04mg/ml, 0.06mg/ml) were chosen for recovery studies. As shown in Table 3, recovery values were between 93.8% and 99.5%. The mean analytical recovery was 96.1%. The relative standard deviation was 3.1%

Table 3 Recovery of β -sitosterol

No.	Concentration added (mg/ml)	Concentration measured (mg/ml)	Rrecovery (%)	Mean Rrecovery (%)	RSD (%)
1	0.019959	0.018729	93.8		
2	0.039918	0.037981	95.1	96.1	3.1
3	0.059876	0.059598	99.5		

Sample analysis. Three solution of jatropha seeds oil (1mg/mL) were determined by the HPLC method, which was prepared as described earlier in the section of sample preparation and extraction. The mean content of free β -sitosterol in jatropha seed oil was 0.33%.

Conclusions

This paper describes a simple HPLC method, to quantitate β -sitosterol with chemical course and material applications. Baseline separation was achieved within a short analysis time using a Waters C18 5 μ m, 250mm $\times$ 4.6mm i.d. column. The quantitation of the stigmasterol was reproducible and the method relative standard deviation is 1.1%. The mean analytical recovery was 96.1%. This simple, rapid, precise and accurate method was successfully applied in the analysis of commercially available jatropha seeds oil. These results therefore indicate that suitable quality control measures need to be implemented to ensure consistent quality and efficacy of marketed products.

Acknowledgements

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A kinetic study on the degradation of erythromycin A in acetone solution with chemical technology

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Keywords: erythromycin A, degradation, kinetics

Abstract. The purpose of this experiment is to know the stability of erythrocin and determine the rate constant by the study of degradation of erythromycin with chemical technology. HPLC method was used for the determination of erythromycin. The degradation of erythromycin are studied at pH=7, pH=8, pH=9 and pH=10 respectively. Experiment results show that the rate of decline of erythromycin followed by pH=10>pH=9>pH=8>pH=7 in the different pH buffer solution. The rate constants are 0.0022h^{-1} and 0.0088h^{-1} at pH=8 and pH=9 respectively.

Introduction

Erythromycin A (EA) is an important macrolide antibiotic used extensively in the treatment of humans and animals. In particular, it is often used in the treatment of penicillin-sensitive patients [1]. Although the literature on the stability of Erythromycin A in acidic aqueous solution is extensive [2], there are comparatively few kinetic studies in basic acetone solution. We investigated the effects of pH (7-10) on the degradation of EA in acetone solution and found that the degradation rate constant with chemical technology.

Material and methods

Reagents and chemicals. Acetone, ammonia water and Ammonium chloride was purchased from the Nan Jing Jian Chen Biotechnology Lt. Cod (NanJing, China). Two reagents used were of analytical grade. Acetonitrile (HPLC Grade) was purchased from Romil Ltd. (The Source, Waterbeach, Cambridge, UK). Erythromycin A was got from East China University of Science and Technology. Water was obtained from a Milli-Q system (Millipore, Bedford, MA, USA) and all samples were filtered using durapore (PVDF) filters purchased from the same source.

Instrumentation and chromatographic conditions. All experiments were performed using a Agilent 1200 HPLC system equipped with a separation module, a DAD detector (model 2996), an online degasser, an autosampler and a Waters C18 Column ($5\mu\text{m}$, $250\text{mm}\times 4.6\text{mm}$ i.d.). The chromatographic elution was accomplished isocratically with a phosphates solution (8.7g dipotassium hydrogen phosphate were added to 1000ml water and 20% phosphoric acid were used to adjust the pH to 8.2) –acetonitrile (40:60 v/v) at a flow rate of 0.8 ml/min. The temperature was maintained at a 35°C and the injection volume was $20\mu\text{L}$. DAD detection was achieved in the range of 200–800 nm, 215nm results were used for quantitative purposes.

Preparation of erythromycin A solution with different PH. The pH of acetone solvent is about 7.0. The pH of acetone solution was adjusted to 8.0 by adding ammonia - ammonium chloride buffer (pH = 8.0). The pH of acetone solution was adjusted to 9.0 by adding ammonia - ammonium chloride buffer (pH = 9.0). The pH of acetone solution was adjusted to 10.0 by adding ammonia - ammonium chloride buffer (pH = 10.0).

Stability experiment. Prepare 5mg/mL of erythromycin A solutions with different pH. Determine the content of erythromycin A solutions at 0 hours, 21 hours, 45 hours, 117 hours and 143 hours respectively by HPLC.

Result and discussion

Degradation of erythromycin A in acetone. As shown in Table.1 and Fig. 1, The content of erythromycin A at pH = 7 changes very slowly. With the pH increased, the change of the content of erythromycin A speeds up. The content of erythromycin A decreases sharply in the buffer solution of pH=10. Experiment results show that the rate of decline of erythromycin followed by pH=10>pH=9>pH=8>pH=7 in the different pH buffer solution.

Table 1 Content of erythromycin A changes with time at different pH

PH	Time (hour)	Content (%)
7	0	46.8
7	21	46.4
7	45	43.8
7	117	50.3
7	143	51.2
8	0	51.2
8	21	48.9
8	45	45.7
8	117	39.1
8	143	37.5
9	0	48.5
9	21	38.7
9	45	29.9
9	117	17.1
9	143	13.3
10	0	13.5
10	21	3.1
10	45	2.1
10	117	2.3
10	143	2.5

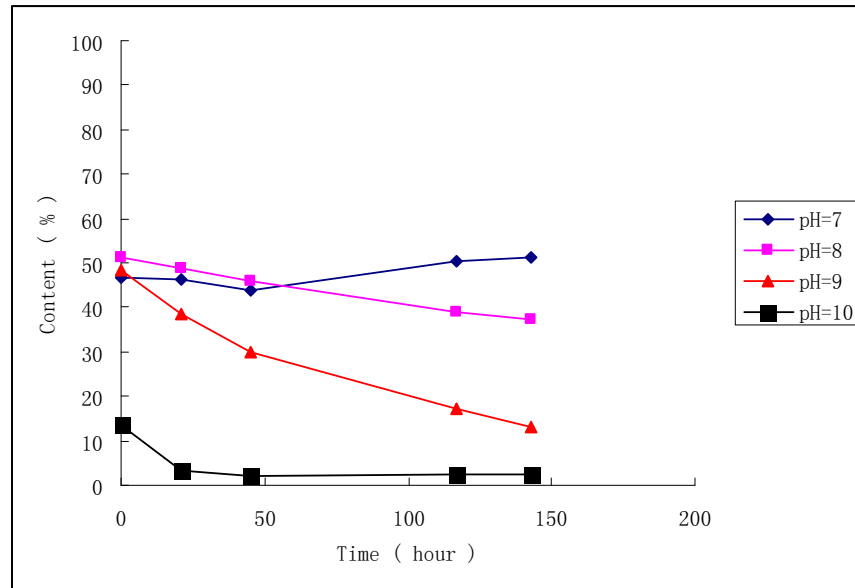


Fig.1 The curve of contents changes with time at different pH

Reaction rate constant. In the pH = 8 and the pH = 9 buffer solution, the content of erythromycin A with time exponentially decreased and it is the characteristics of first order reaction. The reaction rate constant k can be calculated by the initial content of erythromycin A (C_0) and the content of erythromycin A at t time (C_t). Erythromycin A degradation experimental data were fitted and found that there is a good linear relationship between the natural logarithm of residual rate of erythromycin A content $\ln(C_0/C_t)$ and time and the correlation coefficient is greater than 0.95. As shown in Fig. 2, The rate constant is 0.0022h^{-1} at pH=8. As shown in Fig. 3, The rate constant is 0.0088h^{-1} at pH=9.

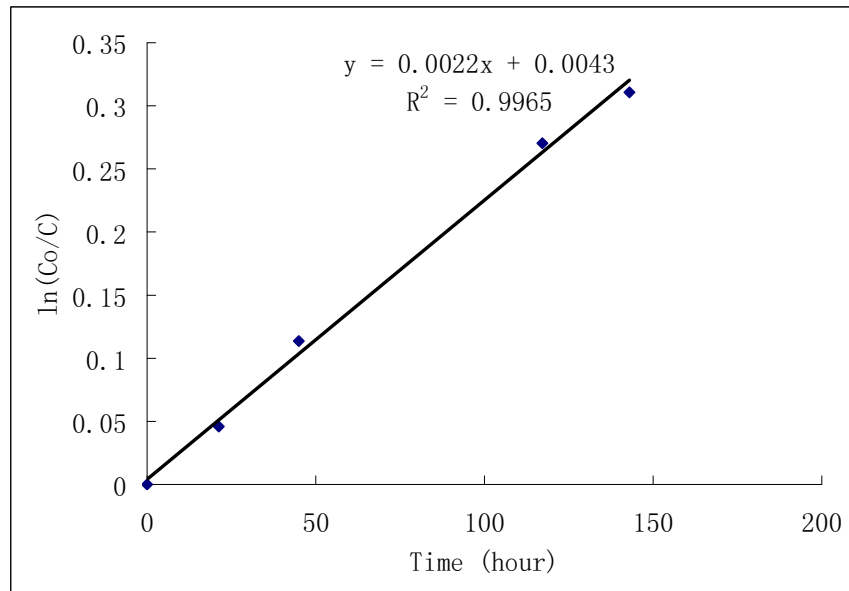


Fig.2 The curve of $\ln(C_0/C)$ changes with time at pH=8

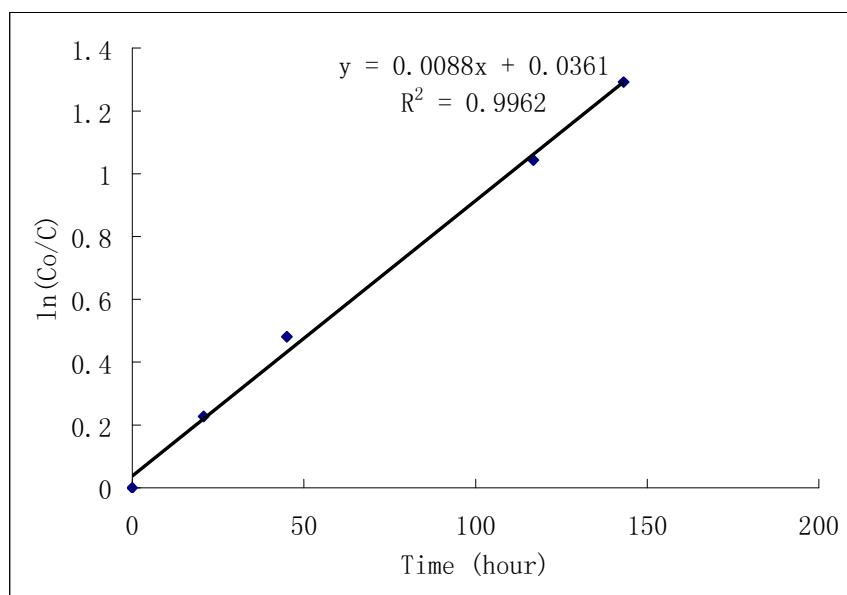


Fig.3 The curve of $\ln(C_0/C)$ changes with time at pH=9

Conclusions

Erythromycin can be stable in acetone solution. The degradation of erythromycin speed up with the increase of the alkaline of solution with chemical technology. The degradation of erythrocin sharply accelerated when the pH of the solution is 10. The rate of decline of erythromycin followed by $\text{pH}=10 > \text{pH}=9 > \text{pH}=8 > \text{pH}=7$ in the different pH buffer solution. The rate constants are 0.0022h^{-1} and 0.0088h^{-1} at pH=8 and pH=9 respectively.

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Extraction of Phytosterols from Jatropha seed oil by the Saponification and Acid hydrolysis method in chemical engineering

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Keywords: Jatropha seed oil, Extraction, Phytosterols

Abstract. In this paper by means of orthogonal array design, the effect of sulphuric acid, time, temperature on the extraction rate of phytosterols was discussed with chemical technology. The optimal parameters for extracting phytosterols of Jatropha oil were as follows: 25g Jatropha oil with 0.25mL sulphuric acid by the 3.5h extraction at 55°C. Under the optimal conditions, the yield of phytosterols was up to 199mg/10g.

Introduction

Jatropha seed oil for the successful development of the biodiesel, provided a strong guarantee for the comprehensive utilization of Jatropha seed oil. It is founded that plants with higher oil content usually also contain more phytosterols. PSs are well-known for their cholesterol lowering properties [1]. International Institute of Nutrition strongly recommended it one of the next ten functional nutrients. Saponification and acid hydrolysis method is more common in the preparation of fatty acid. Currently, some people use this method for the preparation of plant sterols. For example, Liang Liu and Gensheng Yang use saponification and acid hydrolysis method to extract rapeseed oil deodorizer distillate [2]. In this study, Jatropha seed oil is as raw material and saponification and acid hydrolysis method is used for extraction of physiologically active substances of plantsterols with chemical technology. it is significant for the comprehensive utilization of Jatropha seed oil.

Material and methods

Plant material. Jatropha seeds were purchased from Guizhou province of China.

Reagents. Potassium hydroxide, 98% concentrated sulfuric acid, anhydrous ethanol, 85% concentrated phosphoric acid and ferric chloride were purchased from the Nan Jing Jian Chen Biotechnology Lt. Cod (NanJing, China). Other reagents used were of analytical grade.

Instrumentation and UV conditions. WJ2000 UV-visible spectrophotometer; KQ-250DB CNC ultrasonic cleaner; GZX-9146MBE based digital blast dryer; several temperature water bath; AL-104 analytical balance. Weigh 25 gram of Jatropha oil in the round bottom flask, by adding potassium hydroxide ethanol solution (0.625 gram of potassium hydroxide dissolved in 12.5 gram of anhydrous ethanol), shaken , placed in 65 °C water bath pot refluxed 1 hour, slowly added 0.2mL concentrated sulfuric acid solution 65 °C 1 hour, the reaction is completed, stop the heating. Stratification, the lower for a mixture of ethanol and water layer, the upper layer of oil containing plant sterols. Extraction of the upper layer was determined by UV spectrophotometry[3].

Effect of extraction parameters on the yield of the extract

Effect of temperature on the yield of the extract. Extraction temperature was set at 45, 55, 65, 75, 85°C, respectively. Ethanol was chosen as solvent and other conditions were the same to those described in effect of solvents on the yield of the extract.

Effect of time on the yield of the extract. Extraction time was set at 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5h, respectively. Ethanol was chosen as solvent and other conditions are the same to those described in effect of solvents on the yield of the extract.

Effect of amount of sulfuric acid on the yield of the extract. Amount of sulfuric acid was set at 0.1, 0.15, 0.2, 0.25, 0.3mL, respectively. Ethanol was chosen as solvent and other conditions are the same to those described in effect of solvents on the yield of the extract.

The optimisation of the experimental conditions. On the basis of single-factor test, an attempt was made to optimize three parameters, which are confirmed to significantly affect the yield of the extract, as extraction temperature, extraction time, amount of sulfuric acid to obtain good yield of phytosterol by orthogonal test. Each of these parameters was varied at three levels: temperature of extraction at 55, 65 and 75°C, time of extraction at 3, 3.5 and 4 h and amount of sulfuric acid at 0.15, 0.2, 0.25mL.

Result and discussion

Assay of effect of extraction temperature on the yield of the extract. To investigate effect of extraction temperature on the yield of phytosterol, a study was conducted by employing different extraction temperatures in the range of 45 to 85°C (Fig. 1). As can be seen, the yield of phytosterol increased with increasing temperature and reached a peak value at 65°C. The percent phytosterol yield inversely decreased after this optimum temperature value. Therefore, 65°C was chosen as optimum extraction temperature.

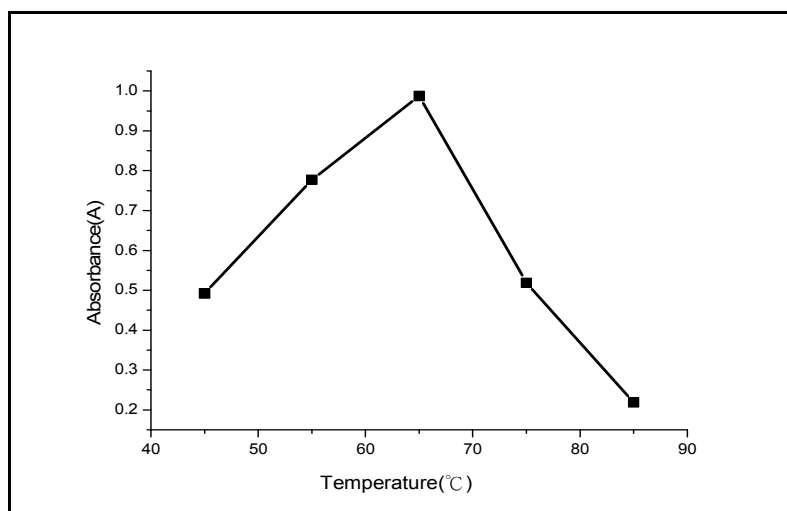


Fig. 1 Effect of temperature on amount of extracted phytosterol using 0.2ml of sulfuric acid for 1h

Assay of effect of extraction time on the yield of the extract. Fig. 2 shows the effect of extraction time on the yield of the extract. Under the given conditions, there was marked correlation between the extraction time and the extraction yield of phytosterol. The absorbance was found to increase from 0.492A to 0.869A when the extraction time increased from 1 to 3.5 h. The absorbance no longer increased with further increase in extraction time, suggesting that when *Jatropha* oil was extracted for 3.5 h, phytosterol contained in oil had been dropped to a minimum value. According to the obtained results, extraction time was chosen between 3 and 4 h for later orthogonal optimisation tests.

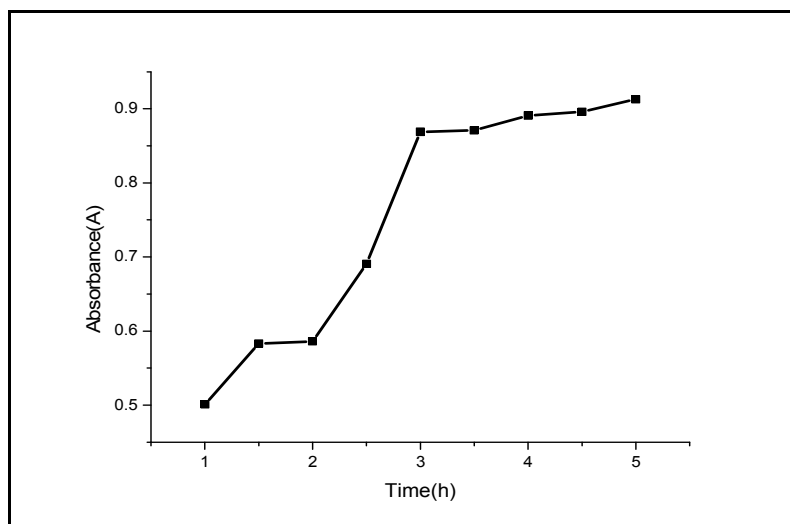


Fig. 2 Effect of time on amount of extracted phytosterol using 0.2ml of sulfuric acid at 65°C

Assay of effect of amount of sulfuric acid on the yield of the extract. The results shown in Figure 3, in 25g *Jatropha* crude oil, 65 °C, 1h under the conditions of acid hydrolysis, the absorbance with the amount of sulfuric acid increases, when sulfuric acid to 0.2 mL, the absorbance decreases rapidly. Therefore, 0.2mL of concentrated sulfuric acid to determine the amount of the sulfuric acid as the best conditions..

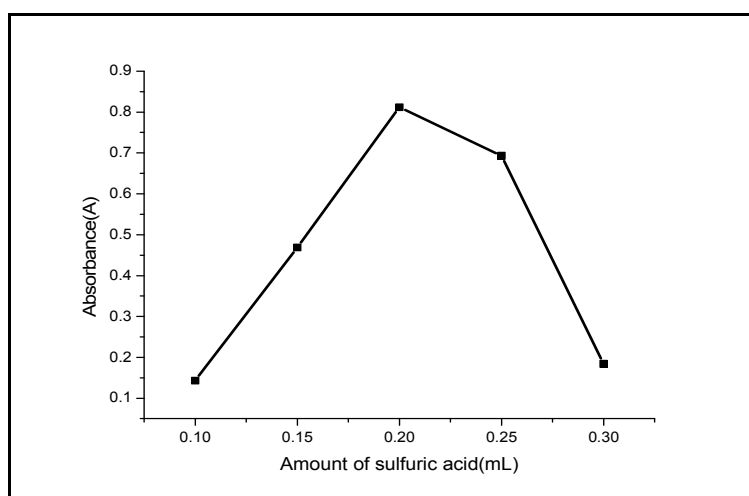


Fig. 3 Effect of amount of sulfuric acid on amount of extracted phytosterol for 1h at 65°C

Optimisation of extraction technology of phytosterol. The three factors (extraction time, extraction temperature and amount of sulfuric acid) were conducted through orthogonal optimization tests under the individual three levels (Table 1). Based on the analytical data obtained in Table 1, the optimal extraction condition was determined as A1B2C3 when all levels of the three factors were considered (Table 1). Therefore, the optimal parameters combinations are as following: temperature 55°C, extraction time 2.5 h, amount of sulfuric acid 0.25mL. Further variance analysis shows that the decreasing order of effect of the three factors on extraction yield of phytosterol were extraction temperature > amount of sulfuric acid > extraction time. The phytosterol extraction yield of three batches of sample was examined under the optimal extraction condition..

Table 1 Optimisation of extraction parameters of phytosterol

No.	Factors			Absorbance
	A	B	C	
1	55	3.0	0.15	0.857
2	65	3.5	0.15	0.835
3	75	4.0	0.15	0.523
4	55	3.5	0.2	1.017
5	65	4.0	0.2	0.824
6	75	3.0	0.2	0.635
7	55	4.0	0.25	1.120
8	65	3.0	0.25	0.745
9	75	3.5	0.25	1.070
K1	1.862	1.738	1.635	
K2	1.817	1.791	1.665	
K3	1.629	1.779	1.708	
R	0.233	0.053	0.170	

A. extraction temperature (°C).

B. extraction time (h).

C. amount of sulfuric acid (mL).

Determination of phytosterols extract. Derived from the orthogonal optimal conditions (55 °C, 0.25mL of concentrated sulfuric acid 3.5h) to extract the acid solution, the three parallel experiments, using UV spectrophotometry extract phytosterols were determined, the measured absorbance degrees are 1.047A, 1.021A and 1.017A, with the average 1.028A. The yield of plantsterols was 199mg/10g.

Conclusions

Concentrated sulfuric acid solution used to increase the polarity of the method to extract the crude oil in the acid hydrolysis of plant sterols with chemical technology, there are three main factors, followed by extraction time, extraction temperature, the amount of sulfuric acid. The optimum conditions for the lab scale liquid extraction were obtained at temperature at 55°C, extraction time of 3.5 h and amount of sulfuric acid 0.25mL. The decreasing order of effect of the three factors on extraction yield of phytosterol were extraction temperature > amount of sulfuric acid > extraction time. Under the optical conditions, the yield of plantsterols was 199mg/10g.

Acknowledgements

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The application of ZR--catalyst on synthesis of polyethylene in chemical engineering

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Keywords: catalyst, UHMWPE, polyethylene

Abstract. A novel catalyst (ZR--catalyst) is prepared in chemical engineering, ZR--catalyst was prepared in a 50L kettle, the repeating property of which is stable. The result of polymerization if a 1m³ kettle connected with a 16m³ kettle is the same as that of the laboratory's activity, the ratio of pollen, and the property of the UHMWPE produced by ZR--catalyst were better than that of the catalyst prepared by grinding method. The molecular weight of UHMWPE prepared with ZR--catalyst is more than 4 million. Meanwhile, the particle is small, uniform and regular. The ratio of pollen of product can be improved by 10 percent.

Introduction

Develop new catalyst, the ethylene polymerization results characterization, and then catalyst preparation amplifier and ethylene pilot amplifier, make used in industrial production. A new method which developed chemical reaction method catalyst, a detailed study of the catalyst components and relevant preparation process parameters on the effect of catalyst of the vinyl polymerization, mainly inspects catalyst preparation conditions and ethylene polymerization process to the income of the form and grain size of UHMWPE influence, further studies to the catalyst performance and product form the main conditions reproducibility and catalyst preparation amplifier and in 1 M3 retained in ethylene polymerization, make used in chemical engineering.

In ZR- -catalyst preparation process, the dosage of the TiCl₄, internal electronic body type, the third component of the type, (improver) thinner kinds and dosage, mixing paste on the performance of the catalyst type has the influence of different level. The right MgCl₂: TiCl ratio for "(Moore ratio), internal electronic the proportion of the body also is so, choose D as ZR--the third component catalyst preparation. Catalyst preparation choose when diluted agent for 120 ml. The propeller stir intensity is high, mixing and dispersing uneven, be helpful for heat and mass transfer, reaction smoothly, preparation of ethylene polymerization catalysts of better performance than with OARS catalyst mixing system. Catalyst preparation autoclave aspect ratio of the system of the catalyst has a significant impact on the particle size, length, and diameter than big system of catalyst powder rate is high. In the same velocity stirring, length, diameter than big kettle length-diameter ratio than a small reactor heat transfer area is large, more important are the big diameter long distance from the kettle materials heat transfer small fast heat. And the catalyst preparation process is basically exothermic reaction, and heat transfer effect is good, the reaction gives heat can be exchanged in time, so the catalyst particles are small.

Polymerization

In 2 M3 polymerization kettle, ZR--with catalyst synthesis UHMWPE, research, the polymerization pressure to the influence of polymerization. Pressure on polymerization polymerization have significant impacts, in polymerization temperature, polymerization time, catalyst concentration and AlEt₃ concentration by the same, the polymerization of catalytic efficiency and pressure of the polymer molecular weight affect see figure 1.

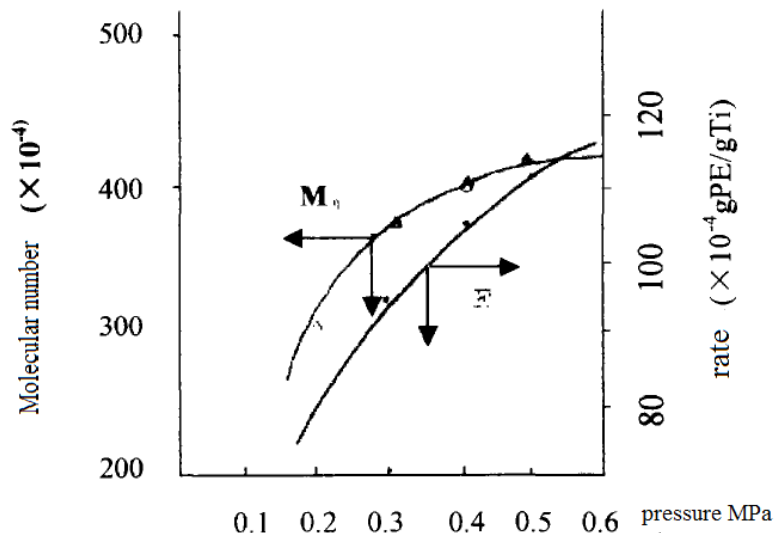


Fig.1. Polyethylene pressure VS the catalytic efficiency

Figure 1 shows that: in the 0.2-0.6 MPa pressure range catalyst efficiency increased the pressure with ethylene and multiplied. Increase the pressure that is increasing in polymerization ethylene thinner the solubility, namely increase monomer concentration, polymerization rate rising rapidly, polymerization rate and ethylene concentration is almost a power relations, so catalyst efficiency increases; As polymerization, increasing the pressure molecular weight increase quickly, ethylene pressures increase, molecular weight increase flattened, for the higher the molecular weight, the greater the concentration of system, the influence of the monomer mass transfer and insert, molecular weight increased slowly.

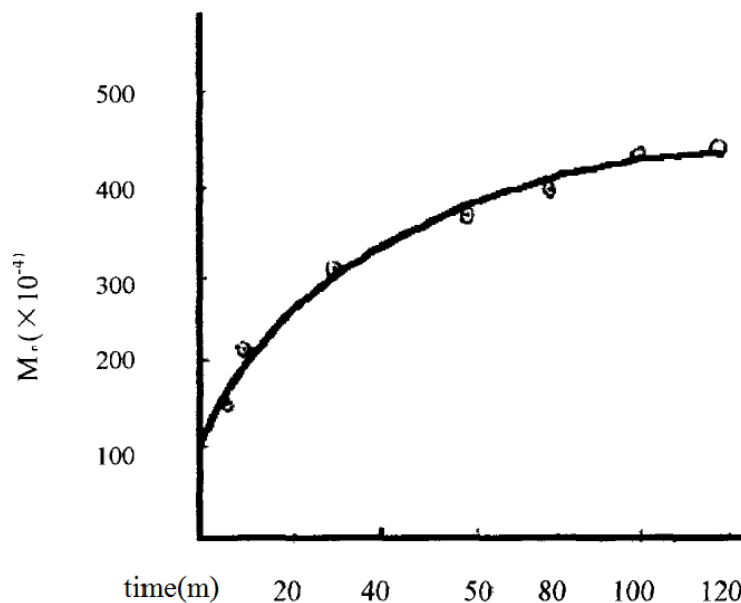


Fig.2. The effect of Polymerization time on polymer molecular weight

Mo Polymerization time increases with the extended, in the initial 20 minutes, Mo Increase quickly, then gradually slow down. Polymerization time is 120 minutes long after, Mo Increase tend to be almost the same ensemble [mentioned, in a polymerization temperature, when a catalyst system (catalyst and help catalyst) must, ethylene pressure on polymerization rate, extended influence polymerization time can increase of MWPE molecular weight, when U ethylene pressure for 0.4 M [Pa, polymerization two hours after UHMWPE basically unchanged. So the molecular weight polymerization time optional for 2 hours.

The conditions of the optimal catalyst and our factory grinding method was with the same process conditions in the catalyst of the lab 1 M3, pilot polymerization kettle of ethylene separately in the pilot polymerization, the test results are as follows: ZR--catalyst for ethylene polymerization income product each main performance indexes are higher than the grinding method catalyst polymerization products, fine powder rate is increased by more than 10%, catalyst efficiency increased by 10%-20%. Equivalent to improve the yield and productivity, visible ZR--catalyst grinding method has more than catalyst significant economic benefits.

The polymer particles morphology

With electronic microscope grinding transmission method and ZR--catalyst of UHMWPE grain shape, the electron micrograph of resin as follows.

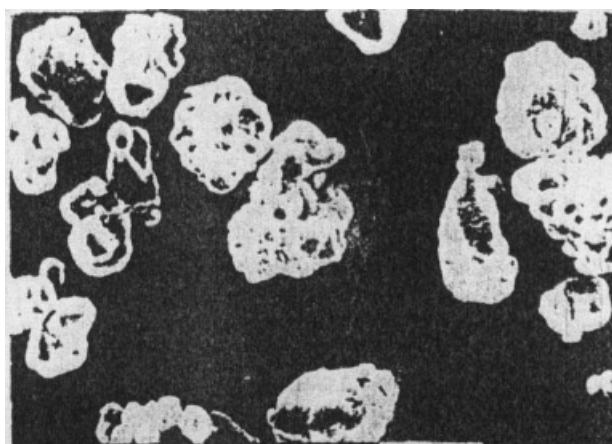


Fig.3. Grinding method of resin catalyst synthesis PE electron micrograph

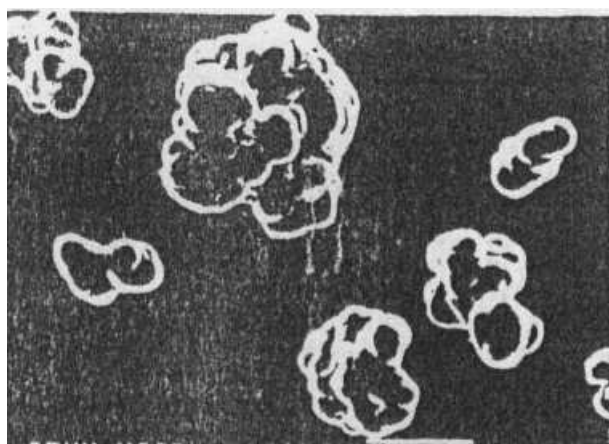


Fig.4. ZR--catalyst polyethylene resin electron micrograph

16 M3 kettle continuous polymerization of UHMWPE resin mixed get product performance test results: ZR--by two kettle catalyst parallel continuous production device assessment, and all the indexes to achieve even more than the original grinding method of catalyst performance index, some properties (such as the impact strength, Rockwell hardness, wear, quantity, etc) are better than the foreign brands of UHMWPE.

Conclusion

The development of the catalyst ZR-catalyst in chemical engineering is from small to enlarge, through 2 M3 and 1 M3 pilot. At 16 M3, double kettle continuous polymerization in parallel in the production line UHMPWE synthesized. The following conclusions are obtained:

1. With response method for ZR--catalyst by the use of the more effective to electronic body compounds and add the third component as a catalyst particles form of development have a kind of practical improver, effective new catalyst has the innovation.

2. ZR--catalyst synthesis routes simple, easy raw materials.
3. ZR--catalyst grinding method than the catalyst polymer particles are small, has uniform neat grain shape, can make the fine powder rate increased by more than 10%.
4. Research, the polymerization conditions on the synthesis of ultra high molecular weight were together the influence of molecular weight, production can produce 3 million, 4 million of the molecular weight of ultra-high molecular weight polyethylene. The catalyst used in industrial production ZR--due to reduced coarse particle of pipeline jams, and reduce the resin glue autoclave phenomenon, continuous operation is good, not only extend the production period, repeat high stability, improve production ability.
5. ZR--catalyst by the production of resin performance than the grinding method of resin catalyst production, performance test shows that alternative grinding method catalyst, and has a significant economic benefit.
6. ZR--the catalyst production of ultra-high molecular weight polyethylene resin exterior shape and performance indicators, all of the same products abroad to quality performance indicators.

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The Research of Active Carbon on the Application of N-propyl Alcohol Reaction in Chemical Engineering

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Keywords: active carbon, n-propyl alcohol, conversion rate, SPC

Abstract. The sulfonated Petroleum coke is used to synthesize n-propyl alcohol(N-PROPYL ALCOHOL) by hydration of ethylene oxide(EO) in chemical engineering and the catalyst of sulfonated Petroleum coke (SPC) is studied. The effect of reactive temperature on the activity of SPC is greatest when reactive temperature goes up, the activity of SPC is quickly enhanced, but when temperature exceeds a certain range, the activity of SPC will reduce; And the activity of SPC will become stronger along with reactive pressure rise, when pressure exceeds a certain value, selectivity of N-PROPYL ALCOHOL will decrease; Also, increasing airspeed will weaken the activity of SPC. The conversion rate of EO reaches 98-100%

Introduction

Petroleum coke of new type high temperature resistant preparation of activated carbon resin solid acid, already use carbon high temperature resistant in chemical engineering, good stability, high specific surface features, and use carbon products are of sulfonic acid groups after in catalytic characteristics, it used as a EO heterogeneous catalytic N-PROPYL ALCOHOL water of the catalyst, through the use of gas chromatography analysis of the product, with the expansion of the conversion and selectivity of the catalyst for investigation, and combining with the stability test and acid catalyst center number of determination, the comprehensive investigation of this catalyst performance. At present the obtained result is: EO conversion rate of up to 98-100%, N-PROPYL ALCOHOL selectivity can amount to 100%.

Start by petroleum coke preparation new high temperature resistant resin solid acid. In this article, the method of thermal sulfonation petroleum coke products are activated carbon, processed, it used as a EO fixed bed catalytic water N-PROPYL ALCOHOL catalyst, through the gas chromatograph analysis of the product, with the expansion of the conversion and selectivity of the catalyst for investigation, and combining with the stability test and acid catalyst center number of determination, the comprehensive investigation of this catalyst performance

The EO homogeneous catalysts water synthesis of N-PROPYL ALCOHOL

- (1) Take about 6.59 (diameter ratio is about 10) has been the catalyst into active carbon products processing in the reactor, the reactor in tubular furnace.
- (2) Pipe furnace temperature to 250 °C, ventilation with nitrogen purge 1.5 hours, the activation and nitrogen protection in the cooling.
- (3) Preparation good EO solution (hydration for 10: than 1), through the metering pump to reactor charging.
- (4) Pipe furnace temperature to the reaction temperature, through the pressure regulator control system pressure, temperature control instrument control temperature, digital house v program temperature instructions.
- (5) With condenser cooling to collect samples, and then gas chromatograph for analysis.

Analysis Method

Qualitative analysis methods: EO catalytic hydration in the mixture contained components are: the EO, H₂O, N-PROPYL ALCOHOL, DEG and TEG, we adopt gas chromatography analysis of the composition of the products. Use GC102 chromatography, PEG20M chromatographic column.

Quantitative analysis method: in the chromatographic operating conditions has determined, and on the basis of the analysis of the validation for guarantee and repeatability and accuracy, we the quantitative analysis for the link and painstaking work. Fixed area normalization method is the advantages of simple, accurate, even though the sample is accurate, the results also without the influence, operating conditions affect the result of the changes are very small, and the results of the experiment in quantitative, it can be as internal standard method to meet the same measurement accuracy requirement, and internal standard method than much more easily.

Result

In this paper, the blank wooden carbon, and different temperature woodiness carbon and products in 25 °C deionized water soaking in 400 after the hr carbon acid sulphonated woodiness center by number, and the results are as follows:

Petroleum coke and wood activated carbon by sulphonate processing, acid number than before the products are center significantly increased, but the change of the products processing temperature acid number no significant influence center. Although products with temperature acid number also increase center, when more than 100 °C temperature products, increasing range is very small. After treatment were petroleum coke and wood activated carbon, 400 after hr after immersing, acid center are lower number, and after immersing, products of different temperature petroleum coke and wood activated carbon acid center almost equal number. So, with the increase of temperature products immerse the loss of acid number before and after the center. Through the comparison also show that blank and treatment of wood activated carbon products of acid number are better than petroleum coke center of activated carbon, first of all this and system of the raw material wood activated carbon. Because, wood activated carbon is lumber after the high temperature carbonization, activation, wood is due by the cellulose of composition, cellulose and contain rich-OH, -COOH etc group, so it made of wood activated carbon acid center than oil of activated carbon number coke. Another possible reason is: wood activated carbon than petroleum coke ash several times higher than the activated carbon, the ash content is mainly inorganic salt or inorganic oxide, which contain more wood activated carbon Lewis acid center.

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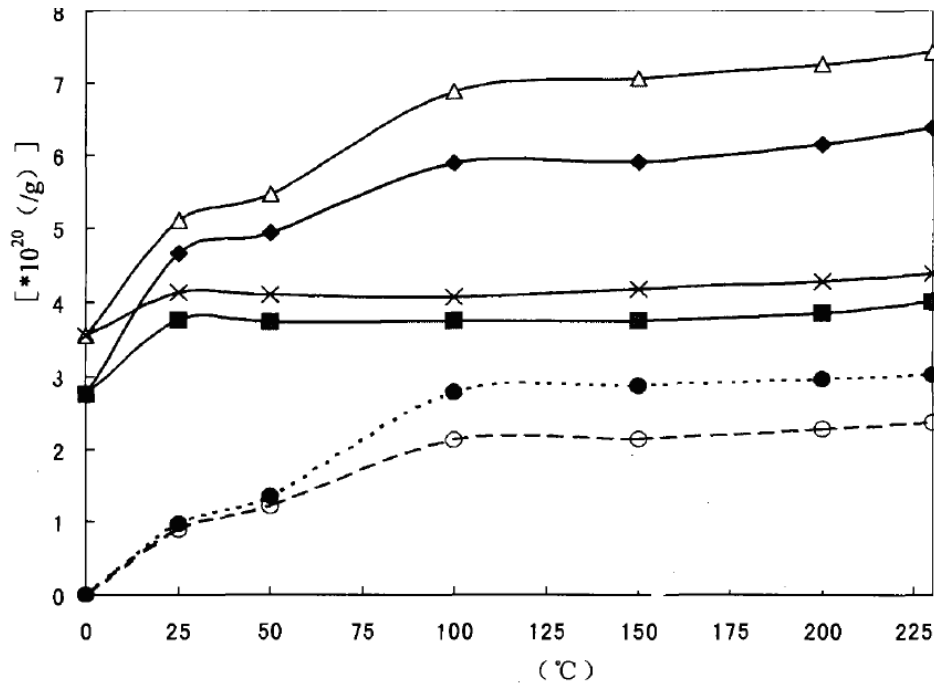


Fig.1 Active acid center contrast

Products of catalytic hydration temperature influence and regularity

Two kind of catalyst in the same reaction conditions, sulfonation temperature changes the influence of catalyst activity and selectivity. Process conditions: the reaction temperature 120 oC respectively, 140 oC, 160 oC, 1800 C, pressure 1. 0MPa, airspeed is 1hr-1, the experiment results are as follows

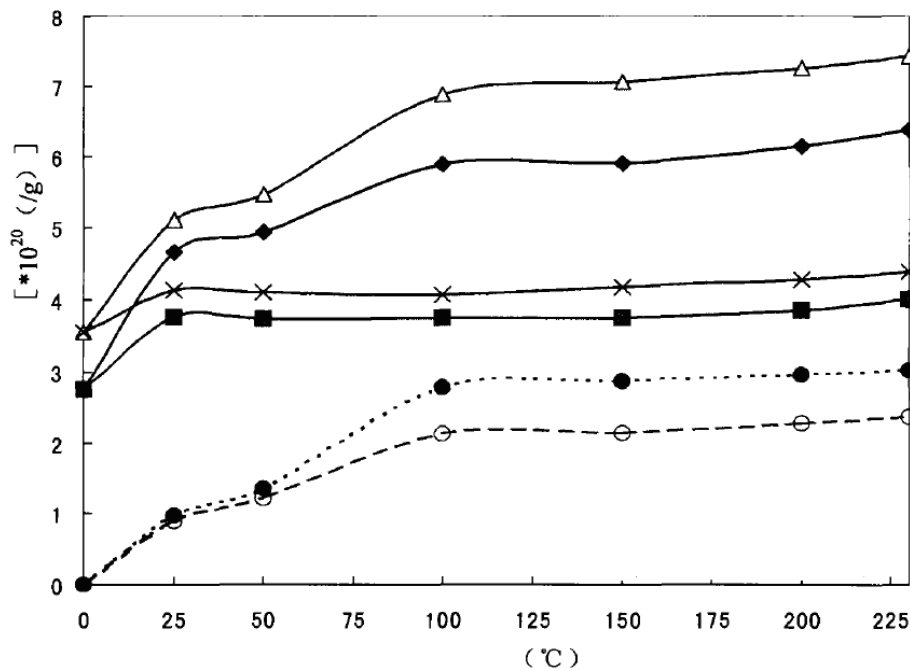


Fig.2 The influence of the temperature on E0 conversion

Products with the increase of temperature, petroleum coke instead of activated carbon catalytic activity has dropped, such as reaction temperature in 120 °C, 25 °C petroleum coke products of activated carbon E0 97.4% conversion, and 230 °C petroleum coke products of activated carbon EO 52.7% conversion. Therefore, petroleum coke in 25 °C or activated carbon 50 °C products under can achieve good catalytic activity.

Low temperature of sulphonated petroleum coke activation reaction temperature range of activated carbon products high temperature significantly greater than the petroleum coke of activated carbon activation reaction temperature range, such as 25 °C, 50 °C petroleum coke activated carbon products

in the reaction temperature is 120 °C 180 °C a, can get good active, EO conversion rate can amount to 90% a 100%; And 200 °C, 230 °C petroleum coke activated carbon products only in reaction temperature is 140 °C ~ 160 °C to keep good active.

After petroleum coke products of activated carbon N-PROPYL ALCOHOL to the selective are better than not petroleum coke products better activated carbon, and are in the reaction temperature 160 °C, the lowest N-PROPYL ALCOHOL selective reach, not in the reaction temperature 140 °C, namely EO conversion rate is highest when, N-PROPYL ALCOHOL selective minimum. The graph still can see, when the reaction temperature over 160 °C, selective and rise gradually, may be EO conversion to reduce. By comparison, it is known that the products of high temperature of the petroleum coke to the selectivity of activated carbon N-PROPYL ALCOHOL products than low temperature of petroleum coke of activated carbon to low, such as reaction temperature 160 °C, 50 °C petroleum coke products for the selectivity of activated carbon N-PROPYL ALCOHOL for 100%, and 230 °C petroleum coke products for the selectivity of activated carbon N-PROPYL ALCOHOL for 97.4%, although 50 °C petroleum coke activated carbon products to EO 230 °C than the conversion of activated carbon products petroleum coke high.

Adding pressure will make EO conversion rate increase, 0.1MPa rose to 0.6 MPa, EO conversion is increased, 0.6 MPa, this trend will slow down. But more than 0.6 MPa pressure, this trend will slow down. N-PROPYL ALCOHOL selectivity also increases, but when more than 0.5 hr-1 airspeed, selective will no longer changes, because is 100%. Pilot increases, EO and catalyst contact time is shortened, the response was not completely, causing the conversion EO Drop, and the selectivity of N-PROPYL ALCOHOL rise.

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The study of Dimethyl maleate CP Synthesized by Strong Acid Cation in chemical engineering

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Keywords: maleic acid, Dimethyl maleate CP, esterification, catalytic distillation

Abstract. The catalytic distillation synthesis of Dimethyl maleate CP by methanol and maleic acid is studied under the application of strong acid cation type catalyst in chemical engineering. The sulfonic resin catalyst is chosen. The reaction of methanol and maleic acid is single one, while that of mono-methyl fumarate chloride and methanol is the reversible reaction balance. The pilot of catalytic distillation synthesis of Dimethyl maleate CP is issued. The best condition for synthesis is proposed.

Introduction

The catalytic distillation tower into a number of reaction period catalyst beds, catalyst beds with steam way of interlinked, catalyst beds connected by catalyst, new catalyst with entrance into the catalyst, used catalyst discharged by catalyst discharged export; Two adjacent catalyst beds have at least a separation between the tray in chemical engineering. Liquid material flow by top down, to the lower part of the rectifying section tray on the liquid pipe down and liquid sealed slot into the lower catalytic reaction period all U bed layer top, then down by gravity flow through the catalyst beds, and under the catalyst to reaction, and the reaction in the reaction of the material is bubble point temperature, reaction heat of vaporization materials by absorption, the reaction temperature constant; By catalyst beds of liquid material flow from the bottom to the lower part of the main fractionators plate, in the tray from the lower part with catalyst beds with steam way of the vapor phase materials heat transfer, mass transfer, heat and mass transfer of liquid materials after the liquid pipe down with liquid sealed slot into the next bed layer to continue reaction. So alternating reaction and the separation process, until the termination or meet the requirements of the reaction so far conversion. Rectifying section of the period, carry fractions tray number and the reaction period of catalyst bed layer, catalyst for content, is based on product purity and yield of reactions conversion, the requirements of the decision.

Esterification catalyst

Catalyst in screening tests is isothermal fixed bed integral of the reactor, the reactor in for Φ 10 x 1.5 mm stainless steel tube, 1.5 m high; Centre for reactor Φ 3 x 0.5 mm of thermocouple temperature tube, used to measure the reactor entrance and exit temperature between any position; The reactor peripherals clip sets. Methanol and shun ester with certain Moore made of raw material with full mixer quickly liquid tank in raw material, the feeding pump measurement to esterification reactor, in sulfonic acid type cation exchange resin under the catalysis of esterification reactor by the reactor temperature of high speed of flow with constant temperature water control, and the temperature control system control and record. Catalyst beds and quartz sand onto the catalyst together, plays the role of hot elimination reactions. The reaction pressure control by pressure regulator is 0.6 MPa (table) to ensure that the reaction in the liquid state. Reaction products are analyzed by the mouth of sampling, reaction products are in the product receiving the tank.

Macro dynamic test

Excessive methanol is beneficial to improve conversion. because of the existence of the water in the product, caused the analysis of methanol has certain error. The regularity of the product of methanol content is better than the ester in regularity, and when alcohol ratio unchanged, the product of certain temperatures methanol content basically airspeed with decreasing, explain the methanol in

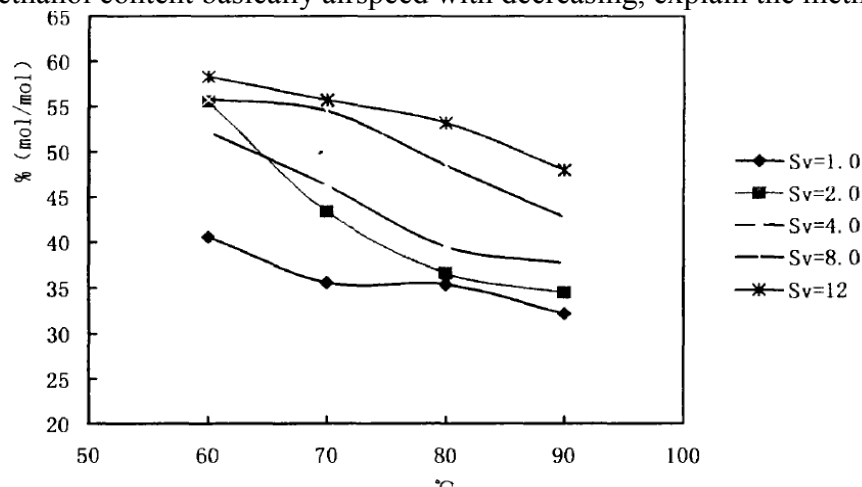


Fig.1. The relationship between methanol Moore percentage content and reaction temperature, the airspeed

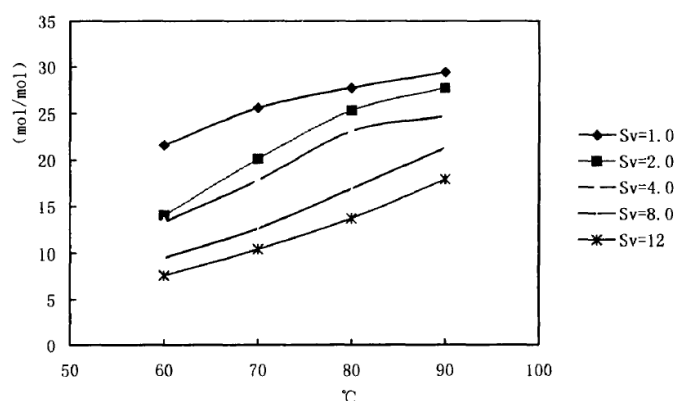


Fig.2. The relationship between double ester Moore percentage content and reaction temperature, the airspeed

reaction in increase: certain product of methanol content airspeed increases with temperature decrease. Dimethyl maleate CP single methyl ester as middle product, on the one hand, the reactions that produce and methanol with single ester, make its content increased; On the other hand single ester and methanol further reaction generated double ester, make its content decrease. The single product increases with temperature and decreases with airspeed. Although the esterification reaction for exothermic reaction, in the investigation of experiment temperature range, high temperature is more advantageous to the single ester into double ester. Trials found at low temperature, airspeed is low, single ester influenced by temperature, its content increases with temperature reduced significantly, and show that reaction is not yet at the thermodynamics balance: at the higher temperature single ester in not effected by temperature, reaction to that thermodynamic equilibrium. Dimethyl maleate CP as dimethyl target product, in the test range of its content increased with temperature, reduce airspeed increased. Pitot high double ester in increased with temperature increased significantly, the lower the content (with temperature increase slowly increase; In less than a (double ester in when by effect is not obvious airspeed, reaction by the influence of the temperature of also is very small, at this time, reaction to thermodynamic equilibrium. To sum up, reaction temperature and conversion to shun ester airspeed and double ester yield greater influence: higher reaction dynamics (by control, double ester in increased with temperature, and shun ester, methanol and single esters content are increased with temperature and reduce; Pitot is lower by thermodynamics balance reaction big effect.

Test equipment and raw materials of the catalytic distillation synthesis of Dimethyl maleate CP

The catalytic distillation synthesis of Dimethyl maleate CP test of the process: the match and with certain Moore methyl than preparation, through the metering pump measurement, preheater preheating, into the reactor, the catalyst in the role of the esterification reaction and reaction temperature clip set by the flow of water in the control, the reaction pressure control system by pressure control, in the reactor, most the ester into Dimethyl maleate CP single methyl ester, part of Dimethyl maleate CP single methyl ester into Dimethyl maleate CP. 2. The reaction product of catalytic distillation tower to continue the esterification reaction, and the produced Dimethyl maleate CP catalytic distillation tower of dimethyl from the bottom of the outflow, excessive methanol and generation of the water out of the top outflow, the pressure control system into condenser cooling, liquid materials into the cooled backflow cans, part of the reflux pump backflow to the tower to another part of the device. The test results show that a, the reaction pressure 0.13 Mpa, reaction temperature 75 °C, the conversion of ester of 100%, Dimethyl maleate CP synthesis of dimethyl yield of 99.5% or more. The catalytic distillation synthetic rubber two dimethyl acid is feasible.

Esterification model

The esterification reaction is operation model of the column RADFRAC simulation, backflow tank top isoperation DECANter simulation model. In ASPENPLUS RADFRAC is a strict model, used for simulation of the various types of multilevel steam a liquid fractionation operation, in addition to the general distillation outside, still include absorption, boiling absorption, the annular stripper again, and boiling the annular stripper, and extraction and were boiling distillation. According to guarantee the reaction of the process of distillation process requirements, the unit operation model RADFRAC DECANter and combined into system simulation process, including a RADFRAC, a DECANter and four strands of logistics. Simulation process, after the confirmation process operation parameters specified, can modeling. Liquid using activity coefficients NRTL models, the gas phase Redlich state equation- Soave Kwong.

Sure module operating conditions (1) unit operation module DECANter according to the esterification reaction distillation process process requirement, input operation temperature and pressure. (2) Unit operation RADFRAC module. According to the esterification reaction distillation process process requirement, the theory of the column board input number (initial value), the incoming board position (initial value), column top pressure, total pressure drop, column top condenser tower heat load and reaction tower number plate for kinetic parameters and can be calculated, all the logistics and the operation unit mass balance, heat balance, composition, temperature and pressure distribution, etc. According to the requirements of the model allows the purity and recovery process indicators such as looking for the optimum process conditions.

The results of simulation optimization calculation

Other operating conditions in the same conditions, with operating pressure increases, reaction temperature increase of the period, Dimethyl maleate CP yield increased. This is mainly because of the rise of reaction temperature, speed up the reaction speed; And for the esterification exothermic reaction, raising temperature against reaction. This is because the catalytic distillation tower reaction district the products constantly move out of the reaction zone, destroy the reaction equilibrium, so as to enhance the conversion of reactant and Dimethyl maleate CP synthesis of dimethyl yield. However, because of the heat resistance performance of the resin catalyst limit, the resin catalyst synthesis of Dimethyl maleate CP reaction temperature cannot exceed resin catalyst

The highest temperature and the catalytic distillation tower to operating pressure of the reaction materials bubble point temperature less than resin catalyst heat temperature.

With the first shares into the increase of the feed, Dimethyl maleate CP synthesis of dimethyl yield decreased; in the same operation conditions, an increase in the reaction of the series can also improve for Dimethyl maleate CP synthesis of dimethyl yield. The first of the increased amount of material reduces the reaction in the residence time of material reaction, and to reduce the Dimethyl maleate CP synthesis of dimethyl yield, which accord with the response of the general rule. In the

same feed into the same operating conditions, an increase in the reaction section of the series, increase the heat and the transfer effect, make the reaction products can effectively remove the reaction zone, destroy the reaction equilibrium, and improve Dimethyl maleate CP synthesis of dimethyl yield.

Along with the increase of the feed into the second shares, Dimethyl maleate CP of dimethyl yield increased. In the first of the feed into the condition of constant, increasing the second shares into the feed will be beneficial to increase the effect of, that is, to one of the reaction products (water) continue to move out of the reaction zone, reduce the reaction zone into the bed of the catalyst reaction materials of content of water, speed up the reaction in the, improve Dimethyl maleate CP synthesis of dimethyl yield. The first stocks of different materials into the feed, increase of the feed into the second of Dimethyl maleate CP synthesis of dimethyl the influence degree of the yield is different also. The second shares into the size of the feed depends upon Dimethyl maleate CP the yield of dimethyl requirement, in Dimethyl maleate CP synthesis of dimethyl yield conditions, the second shares into shoes as low as possible, in order to save the energy consumption of the downstream device.

Along with the increase of flow back, Dimethyl maleate CP of dimethyl yield increased. Increase the flow back to help add methanol in response the content of period, as well as reduce the water content, so to speed up the reaction rate and improve the Dimethyl maleate CP synthesis of dimethyl yield. Back to the size of the overhead product depends on the flow of a Dimethyl maleate CP synthesis of dimethyl content, Dimethyl maleate CP the yield of dimethyl requirement, in Dimethyl maleate CP synthesis of dimethyl yield the requirement, back to flow as low as possible, in order to save the energy consumption of the device in chemical engineering.

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The study of Epoxidation of allyl chloride catalyzed by silica-based HTMS-3A in chemical engineering

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Keywords: epoxidation, allyl chloride, epichlorohydrin

Abstract. Epoxidation of allyl chloride catalyzed by silica-based HTMS-3A was studied in chemical engineering. Under the selected conditions, the conversion of allyl chloride reached 65.6%, the yield and selectivity of epichlorohydrin were 63.9% and 97.6%, the yield of glycerol and heavier by-products were 1.5% and 0.2% respectively. The stability of silica-based HTMS-3A in epoxidation of allyl chloride was studied: the conversion of allyl chloride decreased from 65.6% to 58.9%. The activity of the deactivated catalyst may be recovered by washing with hot acetone, or by calcinations.

Introduction

This subject is to be squeezed in the article the method of forming the preparation of a type load TS 1 catalyst of epoxy allyl chloride laboratory research, solve the molecular sieve grain size small, recycling, the difficult question, improve epichlorohydrin and chlorine propanediol yield, lower high boiling point by-products, using the technology for production of epichlorohydrin industrialization in chemical engineering.

The synthesis of HTMS-3A

25 g sour b cool (TEOS) soluble in 10 g isopropyl alcohol, which drops to add 30 g 20 %-25% of the four propyl oxyhydrogen HuaQian (TPAOH) solution, strong mixing hydrolysis; Will the quantitative qin acid d cool (TBOT) soluble in 5 a 10 g isopropyl alcohol, in 273 K, nitrogen protection, will add to the above flowers TBOT solution of TEOS hydrolyzed, strictly control the drops of acceleration, lest appear turbid. 14 g TPAOH drops are into the clear liquid. Gradually heating up to 348 a 353 K, cast alcohol, and add water to 160 g. Took the solution in 443 K, born under pressure from the crystallization, 3 to 4 days to molecular sieve powders, in 823 K down roasting 6 h, and then have a finished product activation TS 1 molecular sieve. Will gHTMS-3A zeolite 4 powder, 1 g white carbon black (hydrophilic), and 0.2 g and 5.15 g field the powder alkaline silicon sol in research in port 20 min grinding, then edge grinding side adding 15% NaOH aqueous solution of 3.2 g, with even group; In the crowded on three times article kneading, income strip of catalyst in 393 K dry under 16 h. Take off after roasting drying sodium, catalyst finished products. The strip of catalyst after dry, add to the pressure in the 500 mL let, put a bar catalyst small nets, to join 200 mL of certain concentration NH₄NO₃ ion exchange solution in 95 °C water mix, every 12 h use deionized water cleaning, add the fresh ion exchange solution, repeat 10-14 times.

The characterization method of HTMS-3A

Element analysis purposes: to determine the quality of the elements and catalyst points, especially the silicon, the amount of sodium, in order to calculate Si/Ti than and make sure the sodium ions removal from the degree. Molecular sieve samples and Australia will of grinding pressure piece or potassium together will molecular sieve samples and liquid paraffin wax mixed grinding even besmear of salt with sodium chloride. Then use infrared spectrometer for analysis. Nitrogen adsorption objective: to test specific surface area, pore distribution and empty volume etc. The samples will first in 573 K bake for 1h, and then in 573 K, 1333.22 Pa vacuum keep 4 h model degassing, to take off the gas in the sample of 77 K liquid nitrogen adsorption test.

Allyl chloride catalytic oxidation of epichlorohydrin

The reaction is lined with polytetrafluoroethylene (PTFE) volume for 50 mL of pressure let the of will and mL acetone, 1.56 g allyl chloride, 2.76 g H₂O₂: (30%), and 0.31 g bar catalyst into the pressure let start time, closed in has been constant temperature after in a certain temperature water, in the electromagnetic stirring, born from the reaction pressure. After the reaction, rapid cooling, filter out the catalyst, analysis of the product.

NaOH content on the catalyst effect on the strength of broken

When NaOH addition amount is low, because the dosage of the water must be, alkali concentration is not high, and there is a large part of the oxidation silicon and TS filling a 1 through the, the particles of the outer surface of the doesn't work, can not reach the glue dissolve effect; When NaOH addition amount of increase, the higher concentration, except with NaOH powder in the hole outside, still have enough NaOH exist in between particles and grain, make each other particles dissolve connection become fully glue; But, when NaOH quantity increased again, the surplus, not dissolve in glue, the ultimate strength of catalyst have no effect.

Bar catalyst hot heavy curve appeared three weightlessness faster temperature range, A representative peak physical adsorption removal from water, peak B is for chemical adsorption removal from water, peak C wider, contains the powder, gesso hetian removal from. Moisture removal too fast, can lead to bar catalyst sharp contraction, the influence of the broken strength; Qing powder material removal field too can make big hole and catalyst increasing, also can cause the decrease in the strength of resistance to broken. But the drying temperature is too low, cause in ion exchange before the adsorption of water in a bar catalyst residual too much, the strength of the catalysts adverse, therefore, will be dry, roasting process is divided into three stages:

- (1) Bar catalyst in room temperature airing, move into the oven temperature gradually from room temperature to 393 K, dry 16 h above;
- (2) Dry sticks of catalyst after thousands of MaFuLu move gradually heating up to 493 K, stay 2 h;
- (3) Continue to heat up to 823 K, roasting 4 h above.

The best article crowded formula for: molecular sieve the content of 64%, 7%-8% NaOH dosage, alkaline silicon sol (solid content 24.0%) amount to 37.0%-39.0%, drying temperature 393 K, roasting temperature points 493 K and 825 K two paragraphs. Using the above article crowded bar catalyst resistance formula income broken intensity as the 15.2 N/mm.

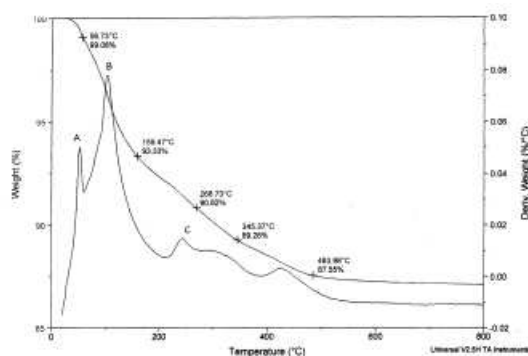


Fig.1. Bar catalyst hot heavy curve

HTMS-3A catalytic oxidation allyl chloride

Do not add allyl chloride other conditions as catalyst (conversion into effective component) 0.29, acetone and mL, hydrogen peroxide 0.026 mol, reaction time 4 h, reaction temperature 318 K blank testing and the pure calibrate acetic acid. Found in blank experimental conditions by a small bit of acetone was oxidized to acetic acid, and at the same condition to join allyl chloride acetone was the reaction of the amount of oxidation because the following two factors will be far less than the blank

experiment. One is because allyl chloride more to oxidation, there exist in HTMS-3A activity center allyl chloride and acetone competition; Second, in the join allyl chloride of the reaction, in the process of the concentration of hydrogen peroxide with reaction in the lower in, and did not add allyl chloride blank experiment the concentration of the hydrogen peroxide almost unchanged.

The comparison of the catalytic activity

The experiment using operated intermittently, allyl chloride epoxy the reaction system of the reactant concentration and product concentration in the reaction process has been a change, allyl chloride conversion, epichlorohydrin yield and selectivity of hydrogen peroxide, the effective utilization and chlorine propylene glycol and high boiling the yield of all things with the length of the reaction time and change. Figure 2 (a) a (d) respectively in pure reflects the HTMS-3A and article crowded the catalyst all variables in the molding with reaction time tendency. The other reaction conditions for: catalyst (conversion into effective component) 0.29, acetone and mL, allyl chloride 0.02 mol, hydrogen peroxide 0.026 mol, reaction temperature 318 K, born from the reaction pressure. along with the extension of reaction time, reaction deeply, allyl chloride conversion rate increase, chlorine propylene glycol and high boiling point by-products increased, epichlorohydrin selective in the peak on a downward trend. From (a) figure can see, in 2, 4, 6, Sh, pure HTMS-3A allyl chloride conversion rate is higher than the bar of catalyst, therefore, a pure TS, allyl chloride catalytic the reaction rate of epoxy than in HTMS-3A / S10: catalysts allyl chloride reaction speed is fast. But from (b) figure that, for pure HTMS-3A and HTMS-3A/510: catalyst, epichlorohydrin is close to the yield. This distinction from (c) and (d) figure can be explained, is pure TS-and HTMS-3A/510: catalysts of epichlorohydrin selectivity, chlorine propylene glycol and high boiling the yield of content, with the reaction of gradually, epichlorohydrin hydrolysis rate and high boiling the generation of things in gradually increasing rate, which produce more of the chlorine propylene glycol and high boiling point by-products, cause of epichlorohydrin selective decline. As mentioned previously, catalyst molding not only can improve the physical properties of the catalyst (such as particle size, mechanical strength), and is likely to affect the catalyst chemical properties (such as catalytic activity and product selective, etc.). Comprehensive (a), (b), and (C), (d) 4 figure can see, in reaction time is 2 h, the two kinds of catalyst reaction get allyl chloride conversion, epichlorohydrin yield and selectivity, chlorine propylene glycol and high boiling point by-products of the recovery are almost the same; With the extension of reaction time, two kind of catalyst on allyl chloride conversion rate is increasing, but the contrast of the article crowded molding catalyst, pure TS a catalyst reaction because of 1 chlorine propylene glycol and yield high boiling things rapidly, and lead to although allyl chloride conversion greatly increased, epichlorohydrin selective but dropped substantially, the result is its comprehensive two catalysts of epichlorohydrin similar yield. When the response time is 4 h, in TS a 1/510: the chlorine propylene glycol and high boiling the yield that there were a low and make epichlorohydrin selective peak, and for pure TS suck, because of chlorine propylene glycol and high boiling the yield of things has increased dramatically reduce the epichlorohydrin and the selective; When the response time is longer (6 h or sh) : catalytic reaction because of chlorine propylene glycol and the generation of high boiling content increases, epichlorohydrin selectivity declined, but the side effects of small speed up speed, and make the of epichlorohydrin yield increased slightly, as for pure TS one, although chlorine propanediol yield increase is not big, but because a large number of high boiling content generation and make of epichlorohydrin selective significantly reduced. Therefore, to improve the article crowded molding of epichlorohydrin selective is favorable.

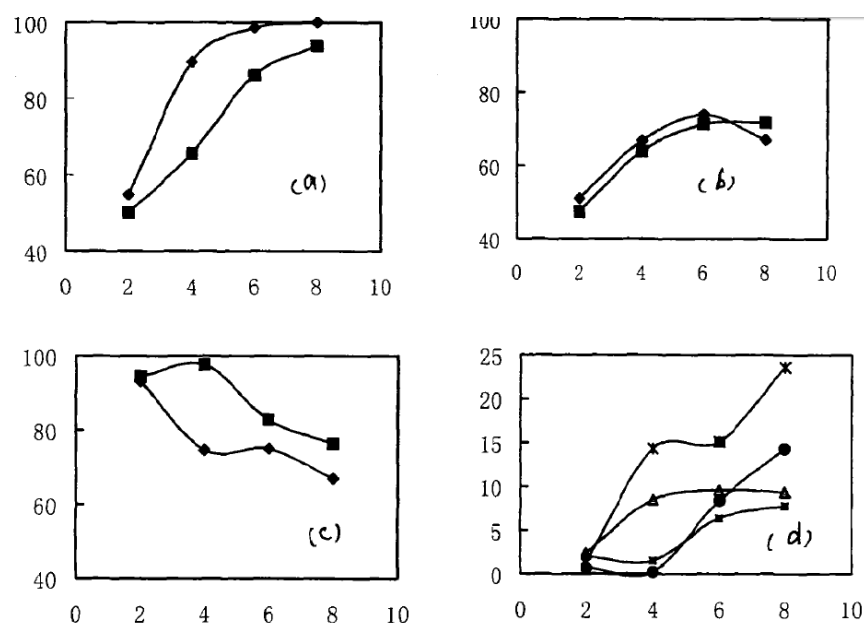


Fig.2. Repsonse time VS Allyl chloride conversion rate etc

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The study of iron catalyst for ammonia synthesis in chemical engineering

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Keywords: iron catalyst, Desorption energy, ammonia synthesis

Abstract. The temperature programmed desorption technique is used to study the hydrogen adsorption on the catalytic surface of fused iron catalysts with different oxide precursors in chemical engineering. The different catalysts desorption active energy, desorped temperature and their amouts desorped have been attained. The desorption energies, desorped temperatures and desorption amounts have been related to the iron ratio ($\text{Fe}^{2+}/\text{Fe}^{3+}$). It is compared with the curve of ammonia synthesis activity against iron ratio. The inhibition of hydrogen in the ammonia synthesis reaction is verified, the adsorption intensity of hydrogen controls the inhibition to nitrogen adsorption.

Introduction

Because the $\text{N}_2 + 3 \text{H}_2 = 2 \text{NH}_3$ process, N: the chemical absorption is considered rate decided to step, this rate steps and work with some more, instead of oxygen in the new system what exactly what play catalyst role, up what kind of effect, still no detailed study. This paper is to study the application of TPD means trying to help the catalyst dosage form chemical adsorption jump of fine structure, and the different phase of the emergence of catalyst with maternal activation energy and activity for the correlation, in order to find out the possible existence of law in chemical engineering. In the TPD process, the first to iron oxides of catalyst pretreatment (restore), get the catalytic activity catalyst clean surface. Then the adsorption of adsorption, after absorption with an inert gas to sweep, then can take off with programs to warming (TPD). This article for the games because of adsorption, therefore reduction after completely, the surface has actually completely for the catalyst that oxygen saturation. So there is no need to go on the adsorption of hydrogen, oxygen in the atmosphere to room temperature cooling with an inert gas purge, and then TPD experiment.

The choice of TPD experimental conditions

The size of the particle size of the catalyst is mainly affect N: in the surface of the catalyst spread within. One of the TPD research aim is to get the H: in the catalyst of the eigenvalue of the surface adsorption kinetic parameters. So it must be in eliminating the spread of the internal and external conditions were determined. This experiment has studied 0.29, 0.49, 0.69 the catalyst TPD experiment. When the catalyst for content of about 0.49 TPD when spectral peak more appropriate, so choose the dosage. And the 0.89 filled amount of relatively reaction tube, it is too big, easy cause temperature difference and then adsorption, because the peak delay phenomenon. If the carrier flow velocity is too large, the thermal conductivity detector has been difficult to detect pool in tail gas concentration changes HZ. When the carrier gas flow velocity over hours, because obviously the peak place again to high temperature direction adsorption, and accompanied by delay phenomenon. So the carrier gas flow velocity over greater than small is not appropriate. Only when the load flow velocity to a certain value, the chart of shape from the carrier gas flow changes to think when the catalyst to spread outside the already basically eliminated, when the carrier gas flow velocity between 10-20 ml/min between peak charts compare the obvious and peak form constant, so this article 16.7 ml/min as carrier gas flow.. This reaction of tube heating rate by electric power used paper necessary limit. The other, on the one hand, electric furnace and reaction between tube by air thermal conductivity, the

greater the heating rate, in the process of temperature catalyst beds of linear temperature, the worse the bed layer temperature uniformity of intensified. So the heating rate also should not be too fast. The temperature of the tube, the reaction is generally $300 \sim 500\text{ }^{\circ}\text{C}$, and at the time of the generation of a gaseous water flow away by's, and to the back of the pipe and the outlet of reactor thermal conductivity pool, if the temperature below $100\text{ }^{\circ}\text{C}$ here, air humidity in May and condensation. This part of condensate in subsequent TPD process will with load flow gradually evaporated, into the thermal conductivity pool. Such income spectrum diagram of TPD is mixed H blade peak signal, but the thermal conductivity pool can only in the thermal conductivity detection in air change, but can't distinguish between water peak signal and the NZ peak signal, and it makes the distortion of spectral peak. So in catalytic reduction process, to prevent the generation of water vapor condensation, control chromatographic furnace box and thermal conductivity temperature $120\text{ }^{\circ}\text{C}$ pool, TPD export pipeline submerged in $120\text{ }^{\circ}\text{C}$ the furnace in the box. H₂ TPD experiment procedure-is: sample in room temperature- $500\text{ }^{\circ}\text{C}$ within a program reduction 5 hours (right now in catalyst has already reached the surface H₂ more saturated adsorption), and then in 2 hours cooling to room temperature, in room temperature with Ar gas purge 2 hours, and then according to different heating rate in room temperature- $700\text{ }^{\circ}\text{C}$ within the H₂-TPD experiment. According to get different samples of different heating rate of H₂-TPD chromatogram, and take off the calculation with activation energy and H₂ off amount with Ed and take off with temperature.

The conclusion

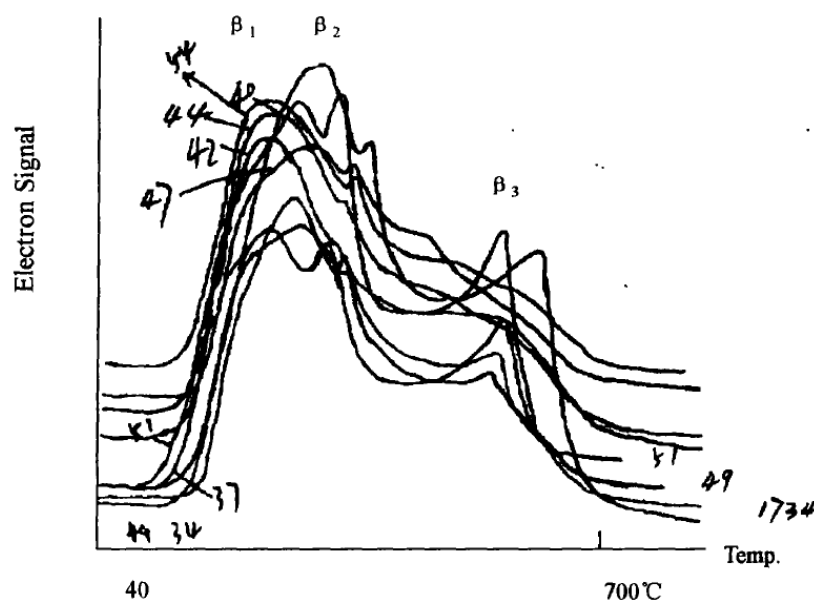


Fig.1. H₂-TPD at The heating rate of 50

It can be obtained:

- (1) All chart of all by three peaks composition, the results show that the catalytic activity on the surface of ammonia synthesis has three different hydrogen sorption state.
- (2) all spectra of the second peak (beta 2) were the first peak (beta 1) covered, which manifested as small shoulder peak, demonstrated that the two peaks corresponding to the activity of sorption state a structure similar to nature.
- (3) With the iron than ($R = \text{Fe}^{2+} / \text{Fe}^{3+}$) increases, can be divided into different nature spectrum diagram of the two groups. When R value in the 0.313-2.16 range, the third peak (beta 3) is very apparent; When R at 3.15-7.54 range, the third peak are not obviously. It shows that the third peak corresponding activity a changed.

(4) For the first peak β 1 small shoulder peak (namely the second peak beta 2) speaking, different than iron range also presents different trend. When iron than R at 0.313-1.11 range, small shoulder peak than increase with the iron is large; When iron than in 2.16-7.54 range in small shoulder peak and than with iron decreases.

(5) To the first peak (beta 1), as all the iron range than the peak place a little change. Explain the first peak corresponding activity with more than a little change of iron.

Based on literatures and analysis, we can draw:

(1) in iron catalyst on the surface of the existing β 1 adsorption, beta 2, beta 3 three sorption state, including β 1 and beta 2 take off with state may be nature of a kind of weak similar chemical sorption state, they correspond a structure similar to the activity of nature; β 3 sorption state take off with the higher temperature, may be a kind of aggrandizement learn sorption state.

(2) Along with the change of the phase composition catalyst matrix, namely with Fe1-xO-the increase of the content of H₂-the TPD the beta 3 peak from strong weak, until vanishing. At that, in Fe1-xO base catalysts are not present in the field to learn the strengthening of the sorption state.

(3) The first peak (beta 1) is likely to come from Fe (111) on the crystal with peak oxygen to take off. Hydrogen in different faces on the absorption of strength according to Fe (111), Fe (100), Fe (110) order from weak to strong, can this from iron single crystal Fe (110), Fe (100), Fe (110) on the crystal faces off with temperature in 400-470 were K (two peak system), 300-350 K (two peak system) and 250 K (three peaks system) can be seen. Also can from Emmett will either iron into two groups and also see in either model, namely the Fe (111) the atomic crystal up loose, can the highest, most active; And Fe (110) on the most closely atomic crystal accumulation, minimum energy and most stable. In addition, from the Fe (111) on the crystal there are three take off with oxygen, while Fe (100), Fe (110) on the crystal faces only two adsorption oxygen. Here you can speculate that the first peak may be Fe (111) on the crystal of oxygen.. The second shoulder peak (beta 2) disappear very may have been the Fe (100) to the Fe (110) crystal crystal transformation. When iron R value than 3.33, maternal started to form vickers body Fe1-xO structure. And the midfielder H₂-TPD spectrum peak also found when R value in the 3.15-7.54 range in the third peak decreased significantly, and at the same time the first peak β 1 relative get big. By N₂-TPD suss out the activity of iron catalyst improve may be due to the Fe (111) faces increasing's sake, therefore probably hydrogen in the Fe (111) on the absorption of crystal is up. Judging from this first hydrogen peak may come from Fe (111) faces.

(4) From TPD spectrum peak change can see vickers the forming process of the body. When FeZ + / Fe3 + at 0.313-2.16 range, spectral peak shape is very similar, with the increase of iron is than, the size of small shoulder peak in the twists and turns. Explain vickers body structure are forming and therefore different alpha Fe faces also gradually formed in. When iron than in 3.15-7.54 range, the third peak becomes not very obvious. From iron and active than the curve can be seen above, the curve is divided into two sections, the first period of Fe2 + / F e3 + in 0.313 1 inside, curve first increased and then drop. The second period of more than 1.0, the curve is always soil liters. As you can see, when iron gradually increased from 1 than to 7.54 activities will be more and more high. And in H₂-TPD chart is the first peak on more and more obvious, so hydrogen in iron catalysts and activity will take off with a certain connection

TPD spectral peak qualitative attribution and analysis

The reduced HZ directly H₂-TPD experiment, add N₂ reactions, purging the after-TPD experiment H₂, and then N₂ reaction, redo HZ a TPD experiment. The experimental results, found that after the first reaction with N₂ peak decreased significantly, and the second peak is obvious move to the right. Add N₂ reactions, the first peak continue to smaller, the second peak to move to the right. Two reactions 1, 2 with the first peak place all the same, the peak size change, because it shows that the nitrogen gas reaction caused the smaller peak oxygen, which can show the first peak really for the hydrogen peak, the second peak also for hydrogen peak, this can be from the location of the peak

basically unchanged can see, because for many times with the take off and caused the second peak peak place of the obvious move to the right, considering the strong adsorption oxygen more difficult to take off the attached, and weaker adsorption of oxygen and nitrogen before the response, so the second hydrogen peak happen move to the right is understandable.

Further has confirmed the first peak (including shoulder peak) is a kind of chemical adsorption than disintegrate, it can and N₂ for chemical reaction, and the third peak is a kind of H₂ aggrandizement learn sorption state, due to the strong adsorption, that he can't through with the reaction from and to eliminate, only make its peak a move to the right, that it can't or not easy to and from the reaction.

In the heating rate for 30 K/min, peak (1) the peak of temperature, in the 170-240 °C, and with iron than increase, peak temperature decreasing trend. From the peak temperature and iron (represents the activity) than the relation curve can see, iron range than in 0.313 1.11 in 0.5 and 1.1 l two points in the place with the lowest temperature off peak, and the activity of these two place within the lowest also. This shows that the strong adsorption hydrogen at this time, the higher the activity, iron range than in 3.15-7.54 range in the general trend of the emergence of hydrogen is also attached with iron temperature of the increase of the ratio of increases, it shows that the hydrogen in the activity on the surface of the adsorption intensity did with the activity of the catalyst have relations. Due to the increase of iron with than,

Wittgenstein gradually formed in the body, and after more than 3.33 than in iron began to form a vickers body, iron exceeded 5.0 later, fully formed vickers body, according to the report with vickers body's formation and its activity on the surface of the Fe (111) faces more and more, from the attached chart of oxygen off can be seen in the first peak gradually change, so the first peak is probably Fe (111) on the crystal of hydrogen to take off with peak, iron range than in 1.1112.16 in a transitional phase right at the situation is different. The third peak because probably not in the main active surface adsorption, so no significant correlation with activity, and the high in iron range than the hydrogen to take off the attached strength also fell. Curve the general trend is to take off the attached strength more and more weak, this and take off the back of the hydrogen with iron and the relationship between the activation energy than corresponds with the curve. In summary, the peak temperature and the correlation than iron, we can draw the first peak oxygen may come from Fe (111) on the take off with crystal hydrogen, and adsorption strength and the activity of iron catalyst has a certain relationship.

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The study of methyl isobutyl ketone(MIBK) synthesis by acetone in chemical engineering

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Keywords: Pd/Al₂O₃, high activity, air velocity, ratio of reactant

Abstract. The catalyst for the reaction was obtained. The high activity, long-life span, stability and application for industry Pd/Al₂O₃ in chemical engineering was issued. The influence of reaction temperature, pressure, air velocity and ratio of reactant for the yield and selection was discussed, and then the optimum condition was determined.

Introduction

Main use is in MIBK boiling point solvents and organic synthetic raw material. As a good performance of solvent, MIBK and commonly used solvent (such as acetone, acetic acid methadone, cyclohexanone, party a and party b ketones), it is characterized by low volatility for good, non-toxic, and other features, is coatings, printing ink, paint, adhesives, epoxy resin. Industries use high-grade solvent, especially as the fine paint solvents MIBK, with flow ping sex good, film hard, volatility for moderate, low viscosity solution and prepared to prevent gel, therefore, in the application of high-grade paint a broad prospect. It lost wax, tape in oil production, metal ore dressing, medicine, atomic absorption spectrometry issues may also have extremely extensive application in chemical engineering.

The experimental method

Catalyst preparation methods: the impregnation method catalyst prepared. Dipping cans for gather atmosphere ethylene plastics cans, packed filter hole boards, capacity for 5 L, ingredients cans of volume for 3L, the use of electronic control temperature drying oven drying catalyst, le blessing in the roasting furnace. Use a fixed bed continuous reaction device in the optimum technological conditions of the experiment, the reactor for 37 X6 white steel tube, the reactor temperature in a thermocouple casing, tubular reactor for external use heat resistance furnace, the use of Japan omron control h_2s table automatic control reaction temperature, 12 point magnetic record catalyst beds and project reactor wall temperature. Use YT-2-4 YT and pressure stabilizer keep the system pressure stable.

The analysis test method

The analysis of chloride: the capacity of the method to determine the content. First determine titration degrees, take 20 mL put the standard solution

Into the 250 mL beaker, join EDTA standard solution 25 mL, diluted the to 60 mL, with 10% NaOH solution moves to a PH = 5, join acetic acid-sodium acetate buffer solution (PH = 5.5-6) 10 m L, two cresol solution (0.2%) 10 drops, with zinc nitrate standard set to a red solution droplets. At the same time be blank test, says take samples in 250 mL beaker, and 60 mL water, heating dissolved, the determination of titration degrees process.

Acetone analysis: using gas chromatography analysis acetone raw materials. Instruments: SP a 501 gas chromatography, the thermal conductivity detector.

Synthetic crude products of water analysis: using gas chromatography analysis of water content in coarse product, instrument, the thermal conductivity detector SP a 501.

Synthetic crude products of the organic matter in analysis: using gas chromatography analysis synthesis thick organic matter content of the product, instrument: GC-8 A hydrogen flame detector.

Catalyst preparation conditions

The pickling liquid determined: with impregnation method for catalyst, usually with active components made it is not the solution, but with the active components of metal soluble salt made into solution soaking. Choice of metal salts should meet the following requirements:

- (1) The roasting process, metal salts of oxide can decompose or by hydrogen reductive into metal.
- (2) The active material of catalysts or harmful substances, in heat or reductive when volatile.
- (3) Active components in the carrier distribution form is different, choose different salt solution.

Pickling liquid PH value of sure: with impregnation method catalyst prepared and deposition in the carrier fine hole pickling liquid and adsorption in the surface of the active components carrier contained in the carrier together. As is known to all, adsorption in the active components and the carrier with carrier is stable and the drying process won't happen in the solute migration, less affected by the conditions of reduction roasting, finally obtained the metal grain tiny, activity than large surface. Instead, deposition in the pores of the active components of pickling liquid, the operation condition the influence is bigger, often happen in subsequent migration and gathered the process of formation, uneven grain, make activity than decrease surface area. Therefore, with the impregnation method catalyst prepared to consider the active components with absorption form as much as possible in the carrier contained.

Through the experiment we determined solution of the PH value of 1-2.

Because we are choosing volume impregnation method such as for catalyst, pickling liquid concentration active group with load measure is different and has become a catalytic dose when preparation, along with the active components increase with load, pickling liquid concentration increased and vice versa. When active components appropriateness must be attached catalyst, with high doses of preparation catalytic changes, pickling liquid concentration unchanged. According to the carrier and the active components water quantity of appropriateness attached, it determine the concentration of dipping 0.1 -1.0 m %.

Reduction of the conditions of the sure: reduction of the preparation of catalysts was the last unit operations. Catalyst reduction is at a certain temperature, reduction in atmosphere; make the process of catalyst activation. Effects of catalyst reduction process are the factors:

- (1) Temperature
- (2) Air speed
- (3) Composition

When the temperature is close to 120 °C, PdCl₂ begin restore, from H₂ consumption visible, reduction of speed, when the temperature reaches 150 °C increases with temperature, H₂ consumption to achieve maximum, restore, highest speed, and, after that, along with the temperature, H₂ consumption slow drop, restore speed down gradually, when the temperature is close to 450 °C at end of reduction. And literature summary, we determined catalyst reduction temperature of 300 °C.

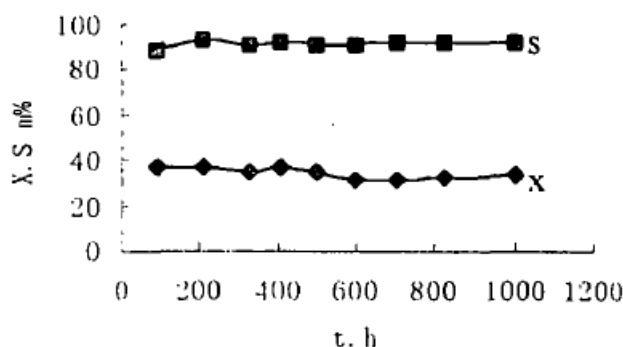


Fig.1 Acetone conversion and selectivity MIBK changes over time

Best technological conditions

Development of the catalyst is a kind of double function that live acid catalyst, in acid and alkali activity center, acetone condensation reaction among heart happened dehydration product happen hydrogenation reaction. The two kinds of active center is made to coordinate the response to complete asynchronous process. Have to study two charge ratio of reactants reaction process influence. Choose acetone conversion and selectivity MIBK for the inspection targets.

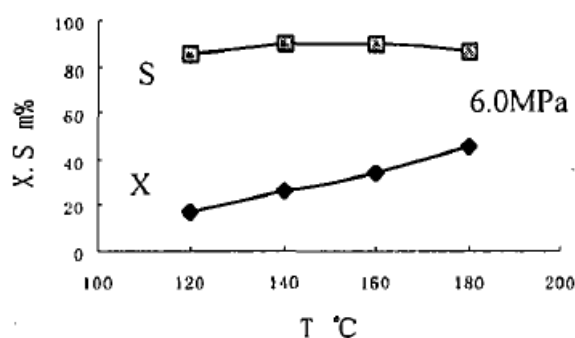


Fig.2. The effects of temperature on conversion and M work in acetone BK selective

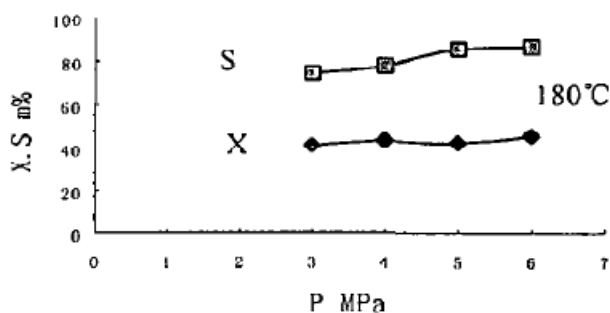


Fig.3. The effects of Pressure on the acetone conversion and selectivity of MIBK

The experiment range, acetone conversion rate increases with temperature increase, 180 °C in the endpoint MIBK obtained when maximum. In the pressure for 4.0 6.0 Mpa range, selective first increases with temperature is rising, and then, with the temperature rise, therefore, MIBK selective in the 140-160 °C scope exists maximum. Pressure is 3.0 Mpa MIBK selective when increases with temperature in the endpoint is reduced, and the 120 °C in maximum.

The changes to the usual acetone conversion reaction law, due to temperature, reaction kinetic energy increase beginning molecules, collision probability increase, the response to an increase, and the reaction speed, making the conversion rate increase, meanwhile that temperature catalytic activity increase. Selective changes, and may be due to the low temperatures, hydrogenation catalyst activity is low, and condensation dehydration function not match, cause MIBK selective low. When the temperature rises, catalyst hydrogenation activity increases, close to the soda acid active center of

asynchronous synergy, MIBK selective rise. To increase the temperature, reaction products and acetone or intermediate products in profound reaction, byproduct formation and intensifies MIBK selective decline. In this paper, by selective take the maximum for target, determine the temperature of 140 °C--160 °C.

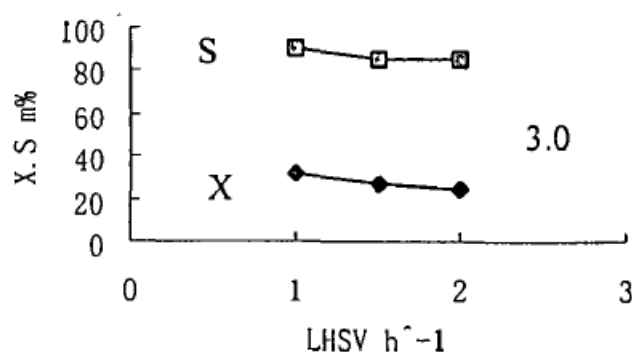


Fig.4. The influence of Acetone liquid on the conversion and selectivity of MIBK

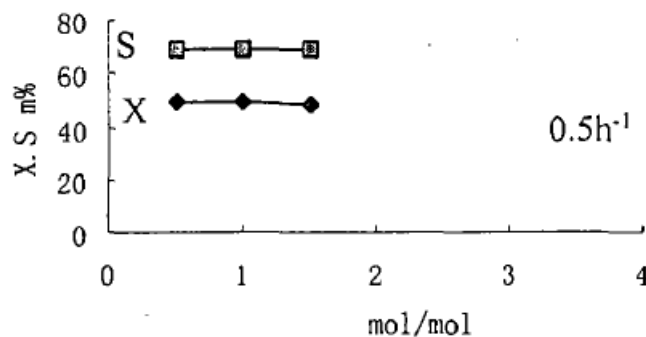


Fig.5. Hydrogen testosterone than conversion and selectivity of acetone MIBK influence

Conclusion

Through the best technological conditions experiment, found the main factors of influence the reaction process for temperature and acetone (liquid, in the range of pressure and hydrogen reaction process testosterone than the impact is not big. Through the analysis of experimental results and discussion, determined the best technological conditions in chemical engineering: Temperature: 140 -160 oC, pressure: 4.0- 5. 0Mpa, acetone liquid air speed: 1.0 h-1, hydrogen testosterone ratio: 2.0 (mol/mol)

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Preparative Separation of Xanthophylls from Corn Gluten Meal by Macroporous Adsorption Resins in Biochemical Engineering

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Keywords: xanthophylls, macroporous adsorption resin, adsorption and separation, corn gluten meal

Abstract: To purify xanthophylls from corn gluten meal by macroporous resins, the static adsorption performance and dynamic separation characteristics of different resins have been evaluated. And SD300 resin offers the best adsorption capacity for xanthophylls than the other resins as HZ816, S8, AB8 and D630. Based on sorption isotherms of SD300, the Freundlich equation was found to fit the experimental data more adequately. Then packed bed column with SD300 resin was used to perform dynamic adsorption and desorption tests to optimize the separation process of xanthophylls. Parameters for adsorption were sample solution xanthophylls concentration 128.9µg/ml, processing volume 11 BV, flow rate 1.0 BV/h, temperature 25°C. After being treated with ethyl acetate, the xanthophylls content in the product was increased to 6.1%, with a recovery yield of 74.0%.

Introduction

Xanthophylls such as lutein and zeaxanthin are naturally occurring yellow–orange oxygenated pigments of the carotenoid family. Being proposed as protecting eyesight, cancer prevention and antioxidation agent, the beneficial effects of xanthophylls have been well documented from the numerous clinical and epidemiological studies in various populations [1-3]. Because the xanthophylls found in the bodies of animals come from their food, and are ultimately derived from plant sources, it is important to prepare xanthophylls from natural compound owing to their unique bioactivity on human healthy [4].

Corn gluten meal (CGM) is a byproduct of corn (maize) processing crude protein. As one of the useful components enriched in the preparation process of corn starch, however, little work has been done on xanthophylls isolation and purification in CGM. In this study, preparation of xanthophylls from corn gluten meal was investigated under static and dynamic conditions. According to their adsorption isotherms and breakthrough curves, behaviors of the adsorbents under two experimental conditions were determined. Then chemical and textural characteristics of the adsorbents and chemical characteristics of the adsorptives were considered with the purpose of elucidating xanthophylls adsorption process.

Experimental

Chemicals

All chemicals used in this work were of analytical reagent grade and used without further purification. The solutions were prepared using water purified in a Milli-Q system from Millipore Co. Ltd. Corn gluten meal was supplied by Hebei Yanshan Corn Starch Chemical Industry Group Co., Ltd. (Yanshan, China).

Various resins including HZ816, S8, AB8 and D630 and SD300 were purchased from Zhejiang Zhengguang Industrial Co. Ltd. (Hangzhou, China). The resins were pre-treated by ethanol, 5% HCl

and 5% NaOH solutions successively to remove the remaining monomers and porogenic agents. Then, it was dried at 60°C under vacuum. Prior to the adsorption experiments, weighed amounts of resins were soaked in aqueous solution.

Preparation of extracts sample solutions

Neutral protease was selected to pretreat corn gluten meal due to the highest reaction activity on xanthophylls. Then methanol was used as solvent for the extraction of xanthophylls after protease hydrolysis treatment. The experimental conditions were determined to be: enzyme load, 14000 U/g substrate, liquid/solid ratio, 20:1; reaction temperature, 40 °C; reaction duration, 5 h.

Static adsorption

The static adsorption tests of xanthophylls from pretreated corn gluten meal were carried out as follows: 5g test resin was put into flask with 100 ml sample solution of waste residue extracts. Then the flask was shaken (120 rpm) for 10 h at a constant temperature of 35°C. Various sample solutions were analyzed before and after adsorption process by HPLC.

Dynamic adsorption and desorption

Dynamic adsorption and desorption experiments were carried out in the glass columns (8mm×600mm) wet-packed with the selected SD300 resin. The packed length of resin bed was 27.9cm. Parameters for adsorption were sample solution xanthophylls concentration 128.9µg/ml, processing volume 11 BV, flow rate 1.0 BV/h, temperature 25°C. After reaching adsorptive equilibrium, the adsorbate-laden column was washed successively with ethyl acetate. During the dynamic adsorption and desorption tests, xanthophylls contents in the effluent liquid were monitored by HPLC analysis.

Results and Discussion

Static adsorption experiment

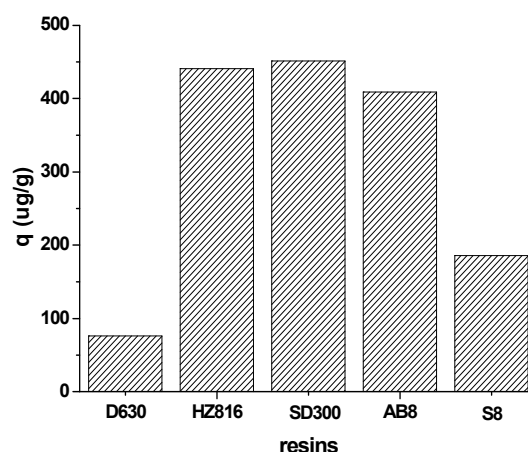


Fig 1 Static adsorption of xanthophylls with various resins

The effects of different resins on xanthophylls adsorption were given in Fig. 1. Comparing the capabilities of each resin with their physic-co-chemical features, it is found that polarity of the resin plays more important role in the adsorption process of xanthophylls. For the non-polar or weak-polar resins of SD300, HZ816 and AB8, their adsorption capacities are much larger than those of polar resins. Therefore, SD300 resin is the desired adsorbent resin with higher adsorption rate for the following separation process.

Adsorption isotherms on SD300 resin

Equilibrium adsorption isotherms on SD300 resin at 25°C were determined under a batch condition (Fig. 2). Then Langmuir and Freundlich models are used to fitting experimental data of SD300 resin. Being indicated from the regression coefficient values (R^2), it can be seen that Langmuir ($R^2=0.9836$) or Freundlich ($R^2=0.9905$) model may sufficiently describe xanthophylls–SD300 resin adsorption, even though the Freundlich isotherm fits the equilibrium data more adequately.

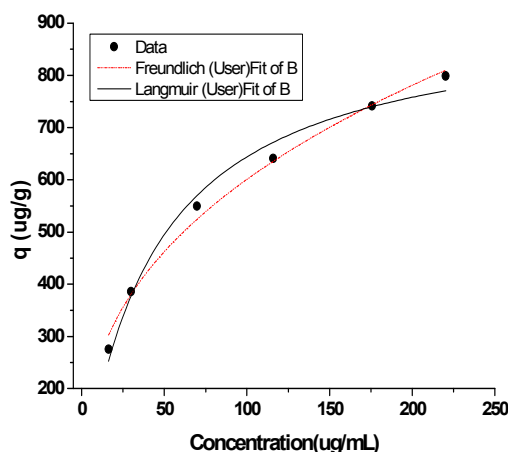


Fig. 2 Equilibrium adsorption isotherms of xanthophylls on SD300 resins at 25°C

Dynamic breakthrough curve on SD300 resin

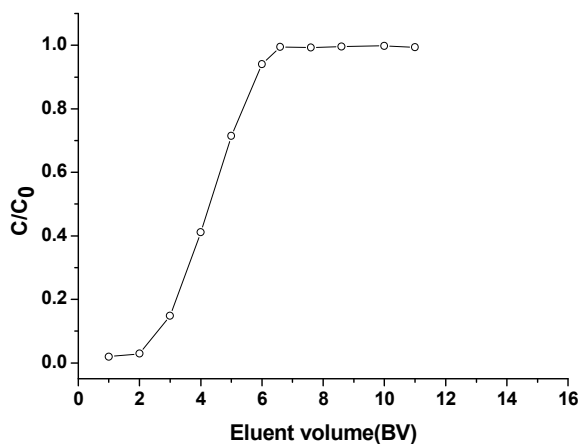


Fig. 3 Breakthrough curves for the sorption of xanthophylls on column packed with SD300 resin at sample flow rate of 1.0 BV/h; $C_0=128.9\mu\text{g/ml}$.

Fig. 3 shows the dynamic breakthrough curves on SD300 resin for xanthophylls by plotting the variation of solute concentration with the effluent volume. The leaking of xanthophylls was found appearing at 2.0 BV under the given experiment conditions. Accordingly, the amounts of xanthophylls passed out during each adsorption step to reach a breakthrough were estimated by volume integrating the outlet xanthophylls content.

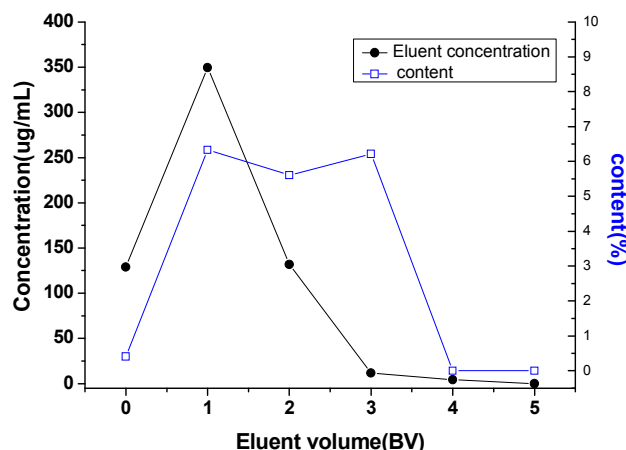


Fig. 4 Dynamic desorption curves of xanthophylls on column packed with SD300 resin at desorption flow rate of 1.0BV/hr; effluent: ethyl acetate.

From the dynamic desorption curve of xanthophylls (Fig. 4), it is found that 3 BV gradient elution of ethyl acetate could completely desorb xanthophylls from SD300 resin. Combining those desorption solutions within the volume range of 0~60 ml, product was obtained by drying them under vacuum. Then the content of xanthophylls reached 6.1% and the recovery yield was 74.0% after one adsorption-desorption turn.

Conclusions

The performance and characterization of five kinds of adsorbents was compared by means of static experiments for xanthophylls separation from corn gluten meal. And SD300, as the non-polar macroporous resins, offers the best adsorption power for xanthophylls among the investigated adsorbent. Then, column packed with SD300 resin was used to perform dynamic adsorption and desorption tests to optimize the separation process. Through one run treatment on the column packed with SD300 resin, the contents of xanthophylls in the product was increased to 6.1%, with a recovery yield of 74.0%.

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Effect of antimony on the corrosion resistance of steel in acid solution with high chloride concentration

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Keywords: antimony; EIS; corrosion resistance

Abstract: This study focused on the effect of antimony on the corrosion resistance of low alloy steel using electrochemical techniques such as dynamic scanning and EIS and immersion test in an acid solution with high chloride concentration. The potentiodynamic test showed the anodic and cathodic corrosion behavior of all specimens and the corrosion rate decreased with increasing antimony addition. EIS showed that the antimony-containing steels had higher rust layer resistance. These test results showed the addition of antimony was convenient to the enhancement of corrosion resistance of the steel in the acid solution with high chloride concentration. The tests proved that the content of antimony controlled to 0.12% in the steel showed the best corrosion resistance.

1. Introduction

Many works had been carried on how to improve the corrosion resistance of the steel which were used under the circumstance of H₂S or CO₂[1-4]. They provided that the corrosion resistance of the steel could be improved by changing the microstructure. Several authors[5-9] have pointed out that the addition of alloy elements such as Cr, Cu, Sn or other alloy elements to the steel could also improve the corrosion resistance in the acid solution. A. Yamamoto's research[10] showed that the mechanism of copper's beneficial effect is based on the suppression of anodic dissolution by elemental copper deposition on the steel surface immersed in the corrosive medium. There were few literatures about the effect of antimony on the corrosion resistance of the steel in the acid solution with high chloride concentration.

The aim of this study was to determine the corrosion performance of antimony-containing steels in an acid solution with high chloride concentration. The corrosion resistance of the steels was characterized by potentiodynamic polarization tests, electrochemical impedance spectroscopy (EIS) measurements, immersion test and corrosion surface micrograph observation.

2. Experimental

The chemical composition of the test steels, in wt.%, was given in Table 1. Only the Sb content differed among the steels.

Table 1 Chemical composition of specimens(%)

specimens	C	Si	Mn	P	Sb	Fe
blank	0.06	0.5	0.65	0.007		balance
1#	0.06	0.5	0.65	0.007	0.075	balance
2#	0.06	0.5	0.65	0.007	0.12	balance
3#	0.06	0.5	0.65	0.007	0.18	balance

The samples that were cut from the cross-section of the rolled steel plate were mounted in epoxy after providing electrical contact to the back side, such that 1 cm² area of the sample was exposed. Before each experiment, the working surfaces of samples were wet ground with SiC paper up to 1500 grit and then degreased with ethanol, cleaned with distilled water, and finally dried in air.

All measurements were carried out in 10%NaCl acid solution, the pH value was adjusted to 0.85 with the hydrogen chloride. Electrochemical measurements consisting of potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) were carried out in a conventional three-electrode electrochemical glass cell with a platinum counter electrode and a saturated calomel electrode (SCE) as reference. The working surface of the sample was 1cm². All the potentials in this paper are reported in the SCE scale. The temperature was maintained at $25 \pm 0.1^\circ\text{C}$. The electrochemical performance of the steels was determined from measurements carried out using a Parstat SS350 system with commercial software program for the AC measurements. The potential of the electrodes was swept at a rate of 1mV/s from an initial potential of the open-circuit potential (OCP) to a final potential of -1000 mV. The anodic polarization test was carried out from the OCP to a final potential when the current density reached to 2mA/cm² at a scanning rate of 1mV/s. After the specimen had reached the stable OCP, the EIS measurements were obtained with an amplitude of 10 mV at frequencies ranging from 100 kHz to 10 mHz. The EIS tests were conducted every 1 h over a period of 5 hours.

Weight loss measurements were carried out according to ASTM G31-71. A hole was drilled in the 60×25×5mm plate for hanging, the specimens were polished with 600-grit SiC paper, degreased in an ultrasonic cleaner with ethanol for 5 min, cleaned with distilled water and dried in hot air. The clean specimen was then stored in a desiccator for 24 h before calculating the area and weighting the initial mass. The corrosion micrograph of the plate was observed under the microscope.

3. Results and discussion

3.1 Potentiodynamic polarization test

Fig. 1 shows the potentiodynamic polarization curves of specimens in acid solution with 10% NaCl and pH value 0.85 at 25°C. Fig. 1(a) shows the cathodic polarization curves. It showed that different Sb-containing steels had same cathodic polarization character. The current density increased with the decreasing of potential. However, the slope of the curves changed with the different addition of antimony. The small addition of antimony had minor effect on the slope by contrast to the blank specimen. With the increase of antimony, the retard effect of the cathodic reaction increased. The effect attained best when the content of antimony was 0.12%. By contrast, when the content of antimony increased continuously to 0.18%, the retard effect of the cathodic reaction decreased. The anodic polarization Fig. 1(b) showed that the tested steels exhibited an active behavior that the anodic current increased with increasing potential, indicating the absence of a passive film on the specimen surface in the acid solution with high chloride concentration. However, the corrosion potential of the steel became positive with the addition of the antimony. The effect became minor when the content reached at 0.12%.It showed that the addition of the antimony was also retard the anodic reaction of the steel in the acid solution with high chloride concentration.

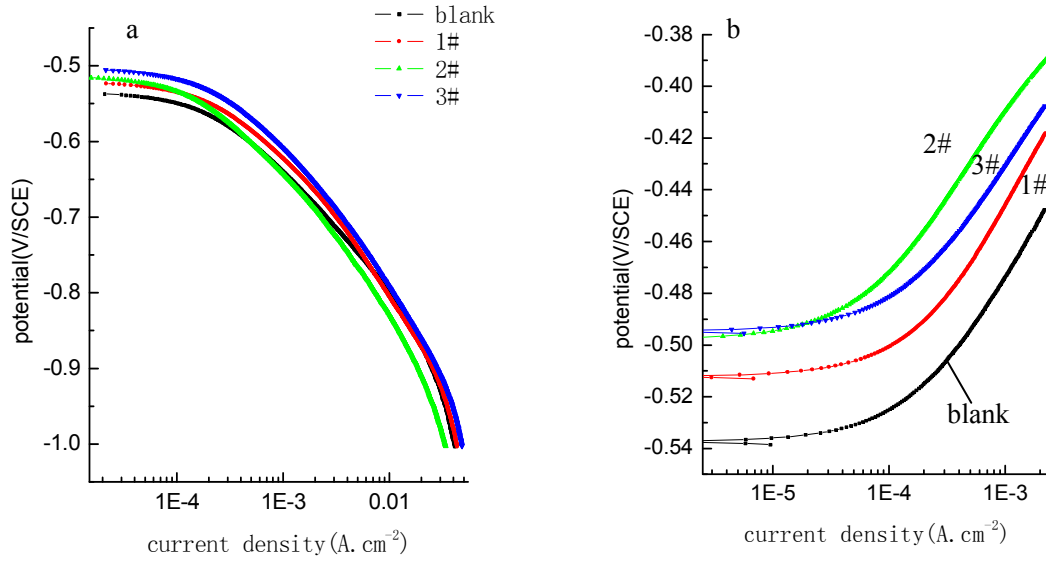


Fig. 1. Potentiodynamic polarization curves of specimens in acid solution with high chloride concentration at 25°C, pH 0.85

(a) cathodic polarization curves (b) anodic polarization curves

3.2 EIS test

Fig. 2 shows the impedance spectra of the Nyquist plot obtained from the steel with

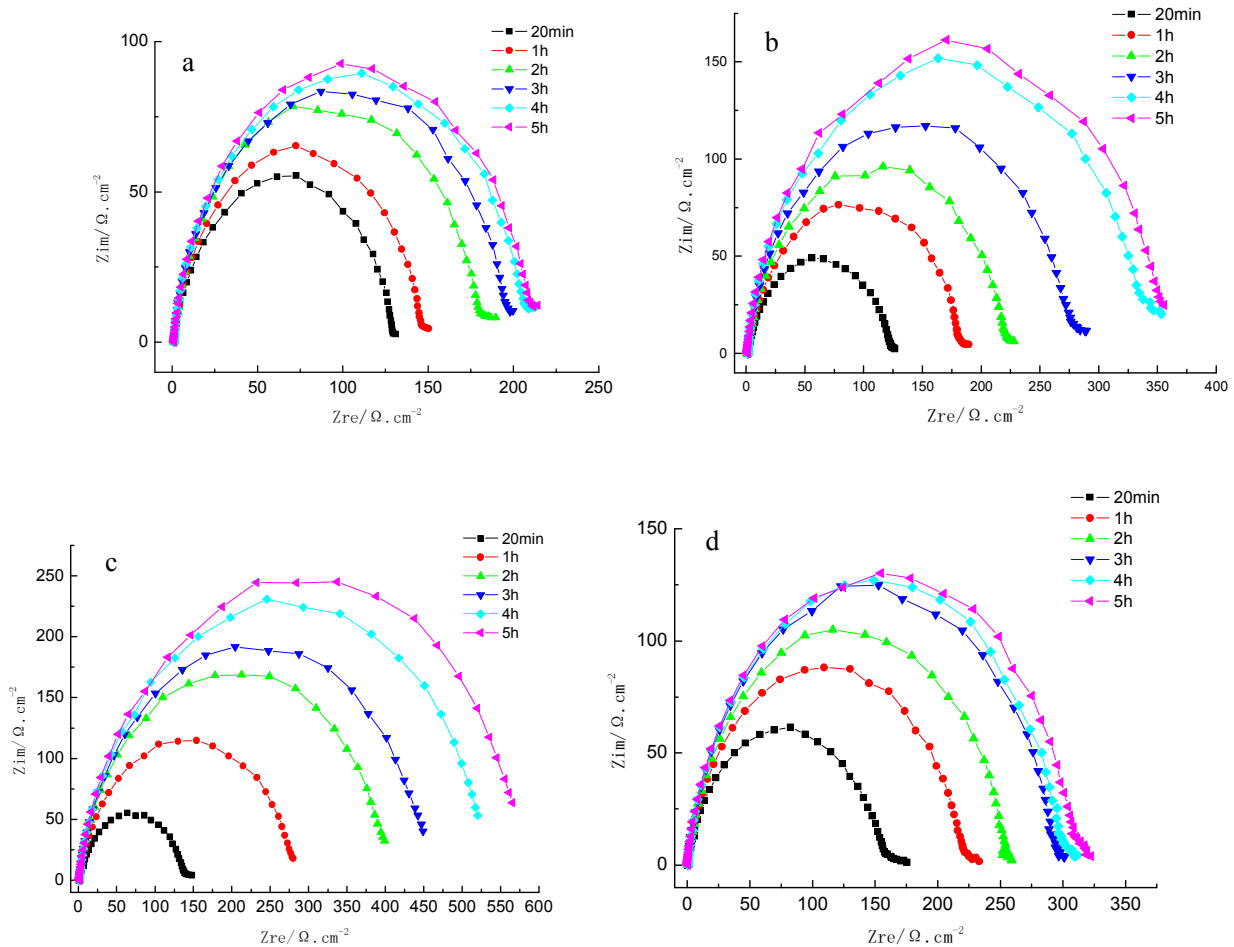


Fig.2. Impedance spectra on the Nyquist plot for low-alloy steels according to Sb content in 10%NaCl, pH 0.85 solution: (a) 0.00% Sb, (b) 0.075% Sb, (c) 0.12% Sb and (d) 0.18% Sb.

different Sb content when immersed in an acid solution with high chloride concentration for 5 hours. The curves took on similar tendency. The diameter of the arc increased with increasing Sb content. However, the diameter of the arc reached the biggest when the Sb content controlled to 0.12%. And the diameter of the arc was increased with the immersion time. These results confirmed the increase in impedance gained via the addition of Sb due to the formation of a protective layer.

Fig.3 showed the relationship of the R_p which derived from Fig.2 and the content of Sb. The results illustrated the R_p increased with the content of Sb and reached to best effect when Sb was 0.12%. It was in accord with the results which showed above.

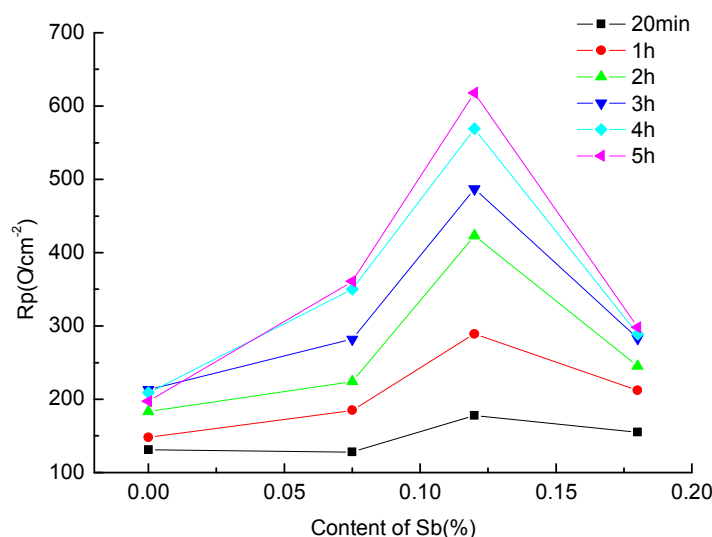


Fig.3 The relationship between R_p and Sb content

3.3 Immersion test

The result of weight loss measurements was showed in table 2. It can be seen that the addition of Sb can reduce the corrosion rate of the steel. After immersion, the weight loss of the steels was ranked in the following order: blank steel > 0.18Sb steel > 0.075Sb steel > 0.12Sb steel.

Table 2 Result of weight loss measurements in acid chloride solution after 72h of immersion.

Specimen	Corrosion rate(mm/y)
Blank steel	2.388
0.075Sb steel	1.64
0.12Sb steel	1.28
0.18Sb steel	1.84

Fig. 4 showed the corrosion micrograph of the steel which had been removed off the corrosion product. The surface of the steel was smooth which suggested an uniform corrosion. The corrosion of the steel containing 0.18% Sb was serious than that the steel containing 0.12% Sb. The reason of this phenomenon perhaps was the grain segregation of Sb.

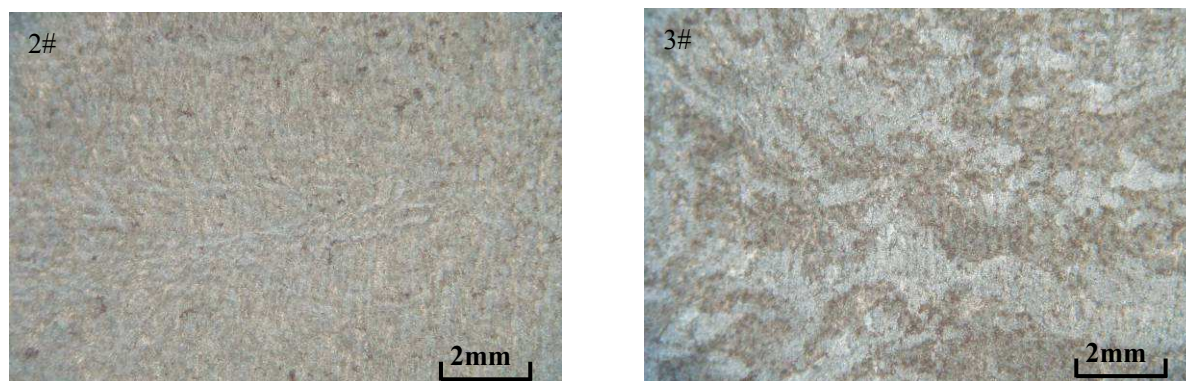
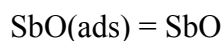
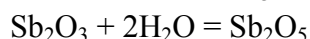


Fig. 4 The corrosion micrograph of the steel after 3 days immersion

From the above experiment results, we can discuss the mechanism of the effect of Sb on the corrosion resistance of the steel in the acid solution with high chloride concentration. In the article[11], the following reactions were proposed to explain the dissolution of Sb in this environment:



This mechanism agreed with the dissolution mechanism of Sb in general acidic media that has been proposed elsewhere. Moreover, the following mechanism was proposed for the formation of Sb_2O_5 on the steel surfaces:



As known, Sb_2O_5 is the thermodynamically stable form of antimony in the presence of oxygen. The corrosion resistance of the steel containing Sb can be improved for the rust layer formed on the surface.

4 Conclusions

The corrosion resistance of the steel in the acid solution with high chloride concentration can be enhanced by adding Sb to the steel. The addition of Sb can retard the cathodic and anodic reaction of the steel. The EIS results also showed that the R_p of the steel increased with the Sb. When the addition of the Sb controlled to 0.12%, the improvement of the corrosion resistance reached best.

Acknowledgement

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The discharge characteristics of PEO films in K_2ZrF_6 with NaH_2PO_4 electrolyte

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Keywords: Plasma electrolytic oxidation; Additives; Potassium fluorozirconate

Abstract: The discharge characteristics of the potassium fluorozirconate electrolyte during plasma electrolytic oxidation process were investigated. Sodium dihydrogen phosphate was applied as additives. Ceramic films were prepared on magnesium alloy in electrolytes with different content additives under constant voltage. The effect of additives on the pH of the electrolyte and the dissolution of the substrate were investigated. It was found that the additives could influence the pH and dissolved magnesium ions effectively.

Introduction

Plasma electrolytic oxidation (PEO) coatings, which are sometimes referred to as micro-arc oxidation coatings or spark/discharge anodic coatings, are formed by the oxidation of metal substrates in aqueous electrolytes, via a series of localized electrical discharge events ^[1]. It is an emerging environmentally friendly technology and has been explored and developed for various applications, particularly those where wear resistance ^[2] and corrosion resistance ^[3] are required. The uniform thickness films can be quickly and easily produced on light metals with complex surface geometry during the PEO process. Because the chemical reaction happens on the substrate surface, rather than by simple physical deposition, the interfacial adhesion is usually better. Most researches focused on the performance of the PEO films, however, the electrolyte characteristics during the PEO process were seldom studied ^[4-13].

In the paper, sodium dihydrogen phosphate was applied as additives. The effect of additives on the properties of the electrolyte such as pH and dissolved magnesium ions were investigated.

Experimental

Preparation of the PEO films

Prior to the oxidation process, AZ31 magnesium alloy sheets with a size of 10 mm × 10 mm × 5 mm (mass fraction: Al 3.1074%, Mn 0.4219%, Zn 0.9075%, balance magnesium) were polished with waterproof abrasive paper up to 2000 grit, followed by degreasing with acetone in an ultrasonic bath and rinsing with distilled water. The power supply was a home-made dc power unit providing voltages of 0-1500 V and a current 0-5 A. Magnesium alloy sample and stainless steel were used as anode and cathode, respectively. Base electrolyte was K_2ZrF_6 with a concentration of 0.025 mol/L. Sodium dihydrogen phosphate were applied as additives to adjust the pH of the base electrolyte. The solution temperature was kept below 40 °C during the oxidation by circulating the cooling

water and by stirring. The voltage was adjusted by the transformer, which was adjusted at roughly the same rate. The samples were treated under the voltage of 460-490 V for 30 min. In this voltage range the discharge was relatively stable. The voltage and the current were recorded with a data acquisition system, the sampling period of the data was 200 ms.

Results and Discussion

The discharge characteristics of K_2ZrF_6 with NaH_2PO_4 electrolyte during the PEO process

The time to reach breakdown voltage could reflect whether the dielectric barrier layer formed more easily or not and the discharge happened more easily or not. The quickly decreased current density suggests that the breaking down of the dielectric barrier layer happened, and then the discharge happened.

The discharge characteristics of K_2ZrF_6 with NaH_2PO_4 electrolyte during the PEO process were shown in Fig. 1. The time to reach breakdown voltage for K_2ZrF_6 electrolyte with 0.0014 mol/L NaH_2PO_4 is about 75 s. And K_2ZrF_6 electrolyte with 0.014 mol/L NaH_2PO_4 to reach the discharge voltage is 10 s. This suggests that it is easy to form the dielectric barrier layer in K_2ZrF_6 electrolyte with 0.0014 mol/L or 0.014 mol/L NaH_2PO_4 . That is to say, the formation of the dielectric barrier layer was easy in K_2ZrF_6 with NaH_2PO_4 electrolyte

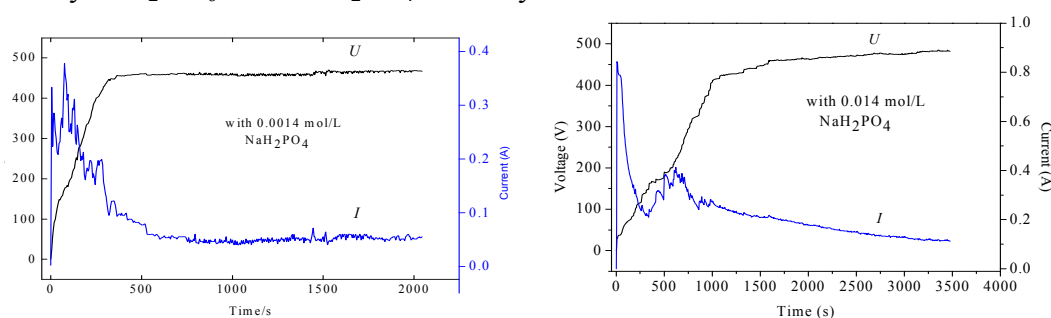


Fig. 1 The discharge characteristics of K_2ZrF_6 and NaH_2PO_4 electrolyte during the PEO process

The effect of NaH_2PO_4 on the pH of the electrolyte after the PEO process

The pH values of the electrolyte after the PEO process with different concentration of NaH_2PO_4 were shown in Fig. 2. It can be found that the pH of the electrolyte after the PEO process is higher than that of before the PEO process. This can ascribe to the reaction of the substrate and the K_2ZrF_6 electrolyte with NaH_2PO_4 . The magnesium can consume H^+ , so the pH of the electrolyte increased after the PEO process. What is more, when the content of NaH_2PO_4 increased, the pH value of the electrolyte before the PEO process tends to be stable. This may owe to the hydrolysis and ionization reaction of $H_2PO_4^-$, which could adjust the pH of the electrolyte, so the pH of the electrolyte before the PEO process tends to be stable.

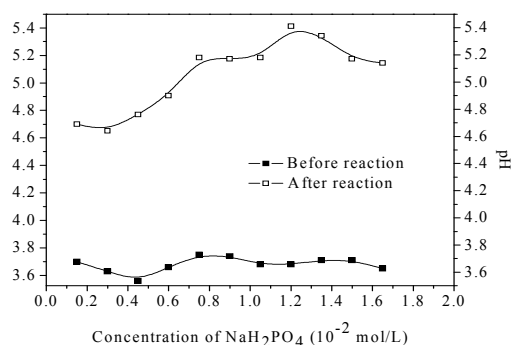


Fig. 2 The pH of the electrolyte after the PEO process with different concentration of NaH_2PO_4

The effect of NaH_2PO_4 on the dissolved magnesium ions of the electrolyte after the PEO process

The content of the dissolved magnesium ions of the electrolyte after the PEO process with different concentration of NaH_2PO_4 was shown in Fig. 3. It can be found that the content of dissolved magnesium ions decreases with the increase of the content of the added NaH_2PO_4 . As the content of the NaH_2PO_4 increased, the pH of the electrolyte changed little (as shown in Fig. 2). This may owe to the hydrolysis and ionization reaction of H_2PO_4^- , which could adjust the pH of the electrolyte. It can be seen that the content of the dissolved magnesium ions decreased with the increase of NaH_2PO_4 . The reason is that the depositions were generated in K_2ZrF_6 with NaH_2PO_4 , which will precipitate in the electrolyte with the general formula $[\text{ZrO}_x(\text{OH})_{4-2x} \cdot y\text{H}_2\text{O}]_n$ during the PEO process.

So the decrease tendency of dissolved magnesium ions tends to be stable.

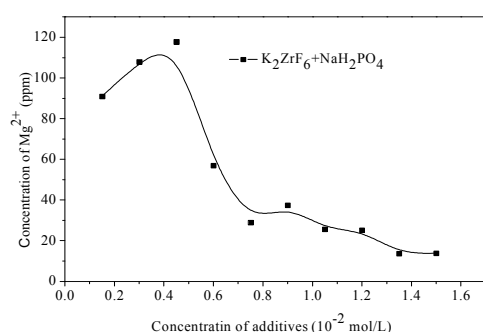


Fig. 3 The content of the dissolved magnesium ions of the electrolyte after PEO process with different concentration of NaH_2PO_4

Conclusions

(1) The discharge characteristics of the potassium fluorozirconate electrolyte during plasma electrolytic oxidation process were investigated.

(2) In the paper, the formation of the dielectric barrier layer was easy in K_2ZrF_6 with NaH_2PO_4 electrolyte.

(3) The content of dissolved magnesium ions decreases with the increase of the content of added NaH_2PO_4 . Depositions will precipitate in the electrolyte with the general formula $[\text{ZrO}_x(\text{OH})_{4-2x} \cdot y\text{H}_2\text{O}]_n$ during the PEO process.

Acknowledgements

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Purification and Biochemical Characterization of Trypsin Inhibitor from Oyster

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Keywords: oyster, trypsin inhibitor, anti-tumor, purification, characterization.

Abstract. In this paper, the purification and biochemical characterization of the endogenous oyster (*Crassostrea gigas*) trypsin inhibitor were researched. A oyster trypsin inhibitor (OTI) has been purified by successive ammonium sulfate precipitation, gel filtration, affinity chromatography and high performance reversed-phase liquid chromatography. OTI has a molecular weight of approximately 5036 Da estimated by high performance size exclusive liquid chromatography. OTI was heat-, acid- and basic-stable competitive trypsin inhibitor. And OTI was double-head inhibitor with the inhibition constant (K_i) value of $1.644 \times 10^{-2} \text{ mmol L}^{-1}$. OTI was composed of nine kinds of amino acid, and rich in cysteine, alanine and glutamic acid. Furthermore, OTI can inhibit the proliferations of human lung adenocarcinoma A549 cell and human cervical cancer Hela cell.

Introduction

Proteinase inhibitors are extensively distributed among microorganisms, plants and animals. Especially trypsin inhibitors from mammalian pancreas and soybean have been widely studied for their physiological roles, inhibitory mechanisms and structures. However, few researches on molluscan trypsin inhibitors are available. Sofina *et al.* found the acid- and heat-stable trypsin inhibitor from the liver of squid (*Berryteuthis magister*) [1]. Faisal *et al.* proved the presence of protease inhibitors in the plasma of eastern (*Crassostrea virginica*) and pacific (*Crassostrea gigas*) oysters. In comparison to *C. virginica*, *C. gigas* plasma exhibited significantly higher specific inhibition levels for trypsin, papain and pepsin. Elsayed *et al.* studied the protease inhibitor in plasma of the softshell clam (*Mya arenaria*). This inhibitor had inhibitory activities against trypsin, papain and pepsin, and also showed the effects of the decrease of disseminated sarcoma. Kishimura *et al.* purified acid- and heat-stable trypsin inhibitor from the hepatopancreas of squid (*Todarodes pacificus*) [2]. The squid trypsin inhibitor with molecular weight (MW) 6300 Da was active against trypsins from the pyloric ceca of starfish (*Asterias amurensis*) and saury (*Cololabis sarus*) and porcine pancreatic. Nagle *et al.* studied the novel molluscan trypsin inhibitor in *Lymnaea* [3]. Margarita *et al.* proved the presence of four trypsin inhibitors in sea anemone (*Radianthus macrodactylus*) [4]. Xue *et al.* purified a serine protease inhibitor from plasma of the eastern oyster (*Crassostrea virginica*) [5]. The inhibitor was a kind of protein with MW 7609 Da, and composed of 71 amino acid with 12 cysteine residues, and its dissociation constants K_i with trypsin, subtilisin A and perikinin were 17.7 nmol L^{-1} , 0.29 nmol L^{-1} and 13.7 nmol L^{-1} , respectively.

Oyster is the most aquacultured species in China, and hence exploring new and creative methods to utilize oyster would be a lucrative and environmentally responsible avenue.

Our laboratory has researched the trypsin inhibitory activity of the pacific oyster (*crassostrea gigas*) hydrolysate with bromelain, and obtained a high active fraction with IC_{50} of 1.894 mg mL^{-1} . In this research work, we have isolated and purified trypsin inhibitor from oyster (*Crassostrea gigas*), and investigated its characteristics with respect to inhibitory activity and anti-tumor activity.

Materials and Methods

Materials. Fresh and lively oysters (*Crassostrea gigas*) were provided by the fish market in Qingdao, China. Trypsin (from bovine pancreas, type II), N-Benzoyl-L-Arginine Ethyl Ester (BAEE), TFA, albumin bovine (V), cytochrome C, bovine pancreas (HPLC, anhydrous) and vitamin B12 were purchased from Sigma Co. (USA).

Preparation of Crude Trypsin Inhibitor. The oyster muscle was homogenized with 0.05 mol L⁻¹ phosphate buffer, pH 7.8 (1:3, w/v), for 3 h at 20 °C. And the homogenate was centrifuged at 8000 × g for 20 min. The supernatant was incubated at 70 °C for 10 min, and then centrifuged at 7000 × g for 20 min. This supernatant was precipitated by ammonium sulfate with 20% and 80% saturation. The precipitate was collected by centrifuging at 7000 × g for 20 min, and then dialyzed in distilled water. Then the dialyzed precipitate was concentrated by lyophilization and used as the crude OTI.

Purification of OTI. The crude OTI was applied to a Sephadex G-75 gel column (25 mm × 500 mm) pre-equilibrated with 0.05 mol L⁻¹ phosphate buffer (pH 7.8), and the protein was eluted with the same buffer. The active peak was carried out on a trypsin-Sepharose 4B column (10 mm × 80 mm) equilibrated with 0.1 mol L⁻¹ phosphate buffer (pH 7.3), containing 0.5 mol L⁻¹ NaCl. The peak with trypsin inhibitory activity was pooled with 0.1 mol L⁻¹ HCl, and then desalted on a Sephadex G-15 gel column (16 mm × 300 mm) equilibrated with super-pure water. The elution profiles were monitored at 280 nm.

The active elution of Sephadex G-15 was further purified using high performance reversed-phase liquid chromatography (HPLC) on a Zorbax SB C₁₈ reversed phase semi-preparative column (9.4 mm × 250 mm) with a linear gradient of acetonitrile (0-40% in 40 min). And the purity was assessed by HPLC using a Zorbax SB C₁₈ reversed phase analytical column (4.6 mm × 250 mm) with a linear gradient of acetonitrile (0-20% in 20 min). The peak with inhibitory activity was lyophilized immediately and used as OTI. The elution profiles were monitored at 225 nm.

Assay of Inhibitory Activity. The inhibitory activity was assayed by measuring the enzymatic activity towards the substrate BAEE [6].

Protein Quantification. The protein concentrations were measured using the method of Lowry *et al.* with bovine serum albumin as the standard protein [7].

Molecular Weight Estimation. The molecular weight of OTI was assessed by HPLC on TSK-GEL G3000 PW_{XL} column (7.8 mm × 300 mm), Albumin bovine (V), cytochrome C, bovine pancreas and vitamin B₁₂ were used as the protein molecular weight (MW) standards, and 0.1% TFA and acetonitrile as the liquid. The elution profiles were monitored at 225 nm.

Stability of Inhibitor Activity against Trypsin.

Effect of Temperature. To evaluate the temperature stability, the solutions of OTI were treated in the water bath for 20 min at different temperatures (20, 40, 60, 80, 100 °C), and then quickly cooled to 20 °C before testing for residual inhibitory activity. The inhibitory activities on trypsin were assayed as described in section 2.4.

Effect of pH. The solutions of OTI were diluted with equal volume of different buffers (0.05 mol L⁻¹): phosphate buffer (pH 2.0, 4.0, 6.0, 8.0) and phosphate-sodium hydroxide buffer (pH 10.0, 12.0). The incubation was lasted for 20 min at room temperature. After that, the pH was adjusted to pH 8.0. The inhibitory activities on trypsin were assayed as described in section 2.4.

Ki Determination. The inhibition constants (*K_i*) of OTI for trypsin were determined from a Lineweaver-Burk plot by measuring the rate of hydrolysis of the substrate BAEE, using trypsin solution of the fixed concentration and mixtures of the same trypsin and two different concentrations of OTI. In the experiment, the rate of reaction is expressed as the reciprocal ultraviolet absorbance value at 253 nm after incubation at 37 °C for 5 min.

Inhibition Curve. OTI solutions with different concentrations were added to trypsin of a fixed concentration (4.2 nmol L^{-1}) at 37°C for 5 min. Residual enzyme activity was measured as indicated in section 2.4 and activities were expressed as the percentage of the highest activity measured. Then the molar ratio was determined by the point which the linear equation was intersected on the abscissa.

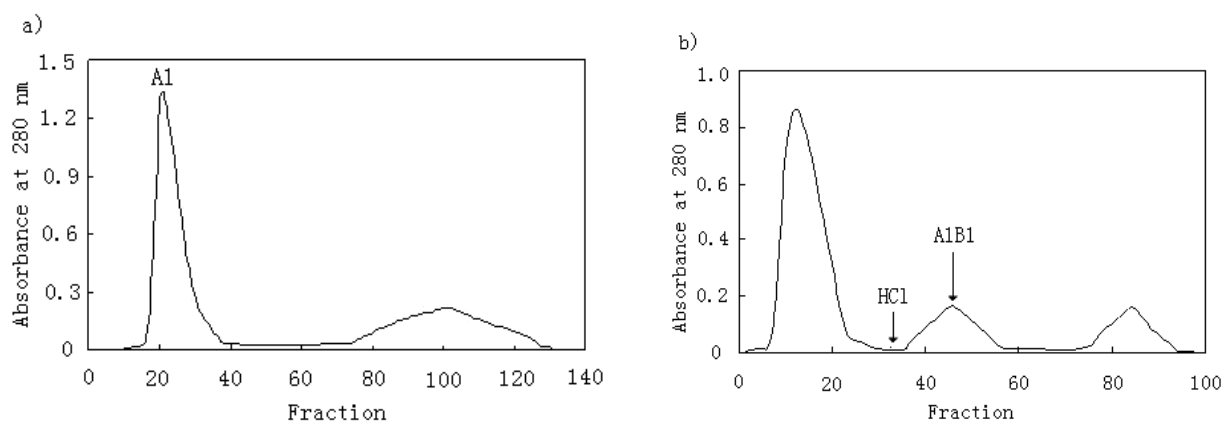
Assay of the Anti-tumor Activity of OTI. The human lung adenocarcinoma A549 cell and human cervical cancer Hela cell were seeded at the density of $1.2 \times 10^4 \text{ mL}^{-1}$ and $7.5 \times 10^3 \text{ mL}^{-1}$ in 96-well plates (180 μL cell suspension per well), respectively. Each group had 4 wells with a non-treated group as control. The cells were incubated at 37°C , 10% CO_2 for 24 h. When the cells anchored to the plates, 20 μL OTI was added to the experimental group, and the equal volume of buffer and anti-tumor medicine 5-fluorouracil solution were put into the control group and the pharmic group, respectively. Then the mixtures were cultured at 37°C , 10% CO_2 for 48 h, and 20 μL MTT (5 mg mL^{-1}) was added to each well and cultured for another 4 h at the same conditions. The supernatant was discarded and 150 μL dimethyl sulfoxide (DMSO) added to the precipitates. When the precipitates were dissolved, the absorbance value (A) was read from auto microplate reader at 570 nm. The cellular proliferation inhibitory rate (R) was calculated using the following formula:

$$R = (1 - \text{Average } A \text{ value in experimental or pharmic group} / \text{Average } A \text{ value in control group}) \times 100\%. \quad (1)$$

Statistical Analysis. All experiments were done more than four times and data are the mean of four assays. The data were first tested for normality and then analyzed with Student t -tests. Statistical analysis was performed using Statistical Program for Social Sciences (SPSS) computer software.

Results

Purification of OTI. The purification of OTI was done by successive steps as follows: extraction in 0.05 mol L^{-1} phosphate buffer (pH 7.8), ammonium sulfate precipitation (20% and 80% saturation), gel filtration on Sephadex G-75, affinity chromatography on trypsin-Sepharose 4B, another gel filtration on Sephadex G-15, HPLC on Zorbax SB C₁₈ reversed phase semi-preparative column and Zorbax SB C₁₈ reversed phase analytical column.



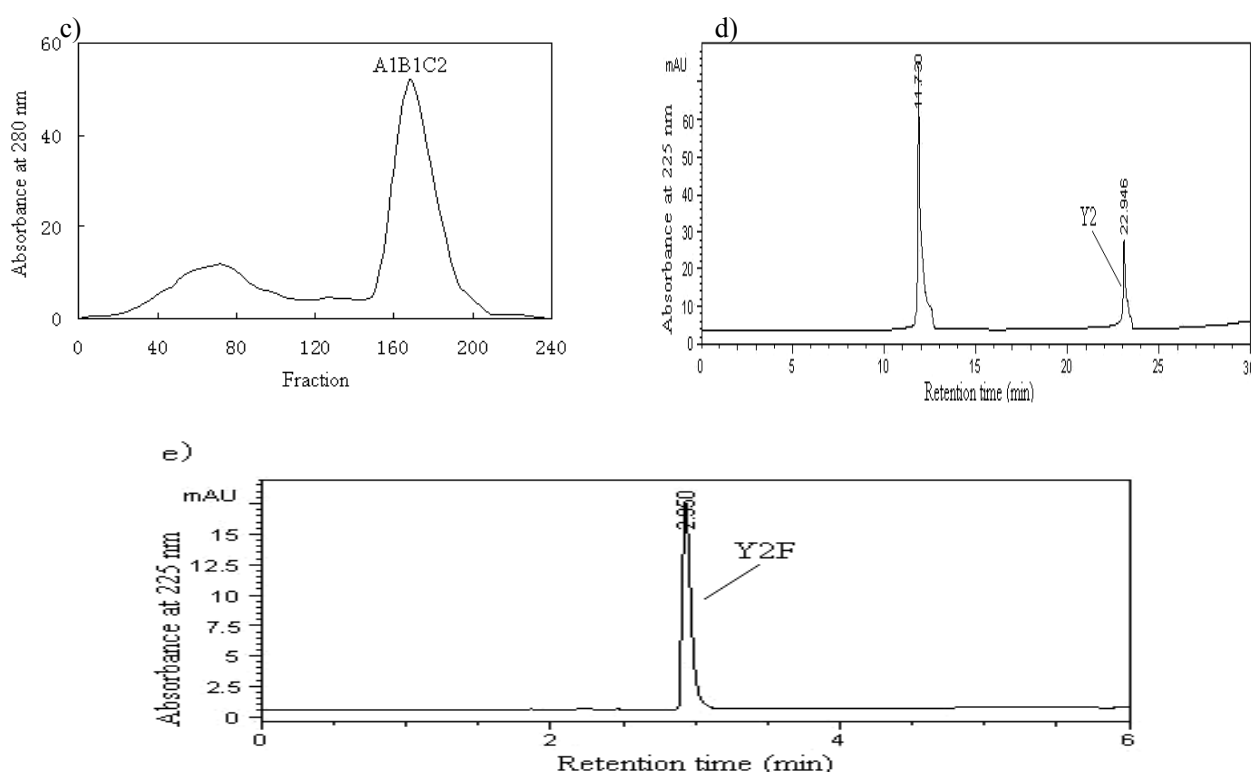


Fig.1 Purification of OTI from oyster (*Crassostrea gigas*)

(a) Gel filtration (Sephadex G-75) of the crude OTI obtained by ammonium sulfate precipitation, equilibrated and eluted with 0.05 mol L⁻¹ phosphate buffer (pH 7.8). Peak A1 displayed the trypsin inhibitory activity. (b) Affinity chromatography (trypsin-Sepharose 4B) of peak A1, equilibrated with 0.1 mol L⁻¹ phosphate buffer (pH 7.3), containing 0.5 mol L⁻¹ NaCl. The active peak A1B1 was eluted with 0.1 mol L⁻¹ HCl. (c) Desalination of peak A1B1 was performed with gel filtration (Sephadex G-15), equilibrated and eluted with super-pure water. The trypsin inhibitory activity was found in peak A1B1C2. (d) Zorbax SB C₁₈ reversed phase semi-preparative HPLC of peak A1B1C2, equilibrated with acetonitrile and eluted with a linear gradient of acetonitrile (0-40% in 40 min). The peak Y2 showed the trypsin inhibitory activity. (e) Zorbax SB C₁₈ reversed phase analytical HPLC of peak Y2, equilibrated with acetonitrile and eluted with a linear gradient of acetonitrile (0-20% in 20 min). The only peak Y2F had the trypsin inhibitory activity.

The first peak A1 of Sephadex G-75 column (Fig.1a) shows the trypsin inhibitory activity. On the affinity column, the peak A1B1 (Fig.1b) was active. Sephadex G-15 gel filtration provided only one active peak A1B1C2 (Fig.1c). Further, on the Zorbax SB C₁₈ reversed phase semi-preparative column, the second peak Y2 (Fig.1d) showed the trypsin inhibitory activity. The peak Y2F had high purity, basing on the only peak (Fig.1e) eluted on the Zorbax SB C₁₈ reversed phase analytical column.

It is proved that the affinity chromatography is very convenient way for isolating the inhibitor. Although the inhibitor might be hydrolyzed by the immobilized trypsin during the purification, the yield of trypsin inhibitory activity suggested that OTI did not undergo the hydrolytic experience. The purified fold was 57.88, and the yield of OTI was 5.81%.

Molecular Weight Estimation. The molecular weight of OTI was estimated as 5036 Da using HPLC on TSK-GEL G3000 PW_{XL} column.

Stability of OTI. The trypsin inhibitory activity was the highest at 20 °C, and the OTI will lost part of its activity with increasing temperature, for example, the OTI lost about 6% of its activity at 40 °C, but the activity of OTI retained more than 50% at up to 100 °C (Fig.2a).

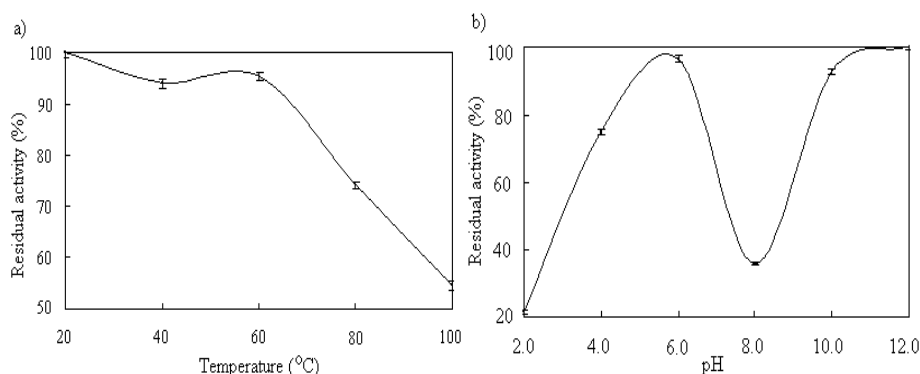


Fig.2 Stability of OTI

(a) Temperature stability of the inhibitory activity of OTI after incubation for 20 min at the indicated temperature. (b) pH stability of OTI after incubation at room temperature for 20 min at the indicated pH.

The pH stability was affected significantly in the pH range 2.0-10.0 for 20 min at room temperature (Fig. 2b). More than 20% of the activity of OTI was retained at pH 2.0, and its activity reduced only about 2% at pH 5.7. There was no loss of activity from pH 11.0 to 12.0, but it is noted that OTI lost about 65% of its activity at pH 8.0.

Ki Determination. Fig.3 illustrates a Lineweaver-Burk plot of OTI for trypsin. It indicated that OTI inactivated the catalytic activity of trypsin competitively. The inhibition constants of different concentrations of OTI were $1.374 \times 10^{-2} \text{ mmol L}^{-1}$ (K_{ib}) and $1.914 \times 10^{-2} \text{ mmol L}^{-1}$ (K_{ic}), respectively, so the inhibition constant (K_i) of OTI was $1.644 \times 10^{-2} \text{ mmol L}^{-1}$. And the trypsin constant (K_m) for the substrate BAEE was $1.211 \text{ mmol L}^{-1}$. As the result, OTI was a competitive trypsin inhibitor with high inhibitory activity.

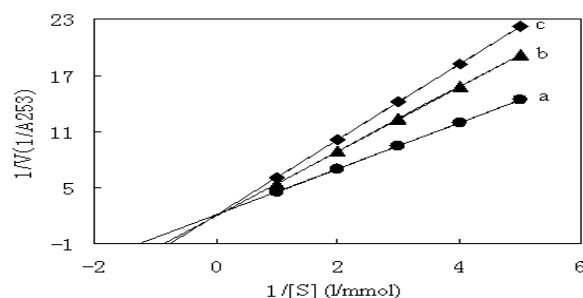


Fig.3 Lineweaver-Burk plots of the hydrolysis by trypsin with and without OTI

(a) trypsin without OTI. (b) trypsin with low concentration of OTI (c) trypsin with high concentration of OTI.

Inhibition Curve. OTI was able to inhibit trypsin in a dose-dependent manner. The calculated molar ratio was 0.5486, namely one molar OTI can inhibit two molar trypsin completely. So it is inferred that OTI obtained here is belongs to the double-head trypsin inhibitor.

Assay of the Anti-tumor Activity of OTI. As showed in Table 1 and Table 2, both of the proliferations of human lung adenocarcinoma A549 cell and human cervical cancer Hela cell were inhibited by OTI, and the inhibitory rates (%) were 20.78 ± 2.37 and 20.68 ± 2.14 , respectively. But the effect on A549 cell was better than another one. And the inhibitory rates of two experimental groups were about 50% of the same dosage of the anti-tumor medicine 5-Fluorouracil.

Table 1 The inhibitory effects of the growth on A549 cells

	control group	experimental group	pharmic group
dosage ($\mu\text{g}\cdot\text{well}$)	—	1.5	1.5
average <i>A</i> value	0.7450 $\pm$ 0.0087	0.5903 $\pm$ 0.0235	0.3957 $\pm$ 0.0146
R (%)	—	20.78 $\pm$ 2.37 *	46.90 $\pm$ 1.37 * •

* $P < 0.005$ as compared with control group; • $P < 0.003$ as compared with experimental group..

Table 2 The inhibitory effects of the growth on Hela cells

	control group	experimental group	pharmic group
dosage ($\mu\text{g}\cdot\text{well}$)	—	1.5	1.5
average <i>A</i> value	0.4080 $\pm$ 0.0036	0.3237 $\pm$ 0.0112	0.2033 $\pm$ 0.0115
R (%)	—	20.68 $\pm$ 2.14 *	50.25 $\pm$ 2.40 * •

* $P < 0.005$ as compared with control group; • $P < 0.002$ as compared with experimental group

Analysis of amino acid composition. The amino acid compositions of OTI was demonstrated. OTI have nine kinds of amino acid, and high contents of cysteine, alanine and glutamic acid. The composition data showed that the content of acidic acid in OTI is more than that of neutral acid, And basic amino acids, lysine and arginine were occurred in low contents.

Conclusion

This study demonstrated the presence of trypsin inhibitor in oyster extracts. OTI was characterized by a molecular weight of 5036 Da in HPSEC. Furthermore, it is assumed that OTI is the double-head inhibitor, because a 1:2 relationship existed between OTI and trypsin. OTI also showed anti-tumor activity against human lung adenocarcinoma A549 cell and human cervical cancer Hela cell.

The present study arouses interest as to whether OTI is distributed only locally in stomach or widely in other tissues probably via serum, and as to whether OTI specifically binds to trypsin and effectively inactivates extracellular proteases released from tumor cells. So, further studies are necessary to elucidate the physiological role of the trypsin inhibitor in oyster.

Acknowledgment

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CHAPTER 3:

Mining Engineering

Fatigue Life Prediction of Buckling String with Cracks in Horizontal Wells of Mining Engineering

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Keywords: horizontal well; buckling; drill string; fatigue life; prediction

Abstract. Fatigue damage in the rotating drill pipe in the horizontal well of mining engineering is usually resulted from cyclic bending stresses caused by the rotation of the pipe especially when it is passing through curved sections or horizontal sections. This paper studies fatigue life prediction method of rotating drill pipe which is considering initial crack in horizontal well of mining engineering. Forman fatigue life prediction model which considering stress ratio is used to predict drill string fatigue life and the corresponding software has been written. The program can be used to calculate the stress of down hole assembly, can predict stress and alternating load in the process of rotating-on bottom. Therefore, establishing buckling string fatigue life prediction model with cracks can be a good reference to both operation and monitor of the drill pipe for mining engineering.

Introduction

With the improvement of the drilling technology, the number of the horizontal well and the extended reach well are increasing, but at the same time, more and more problems of drilling equipment failure come out. The survey shows that 14% of the oil and gas well appearing accidents of drill string fracture, and 80% of the drill string failure caused by fatigue at abroad^[1]. Understanding the mechanism analysis of drill string fatigue failure, establishing the actual fatigue life prediction model, the drill string fatigue life prediction model has an important significance to prevent and reduce fracture accident for the string underground^[2-4].

In the conditions of actual drilling, the drill string is in compression state. The drill string sine buckling or spiral buckling caused by heavy axial load, even leading to be locked^[2,3]. Buckling drill string's shape changes in the well, increasing the pressure between the drill string and the walls, this leads to the drag-torque increases and has great effects to the fatigue life of drill string. This paper analyzes the rule of drag-torque distribution between the wall and the bending drill string, and finally establishes the horizontal well drilling string fatigue life prediction model.

In the process of rotating-on bottom, the well bore is filled with fluid. The string undertakes a variety of force, such as gravity, buoyancy, lateral force and friction force, liquid viscous resistance, etc. Meanwhile, accompanied by temperature increase, buckling and axial deformation.

1 String tension-torque differential equations

The string has three kinds of state that are stability, sine buckling and spiral buckling in the wellbore. Because that contact pressure of the sin buckling between the tubing string and casing is much less than spiral buckling, and there is no more appropriate calculation method, therefore, for the time being using steady state instead sine buckling state. If the tubing string happens to spiral buckling, we need to consider additional resistance and torque^[5-7].

At the upper of spiral buckling string, there may be torque in this section, because of the spiral buckling, and the farther away from the buckling string the smaller value, and its distribution is not clear, but as we know the value becomes zero at the wellhead. Assuming that reduced torque is proportional to positive pressure, and the torque turns to zero at the wellhead.

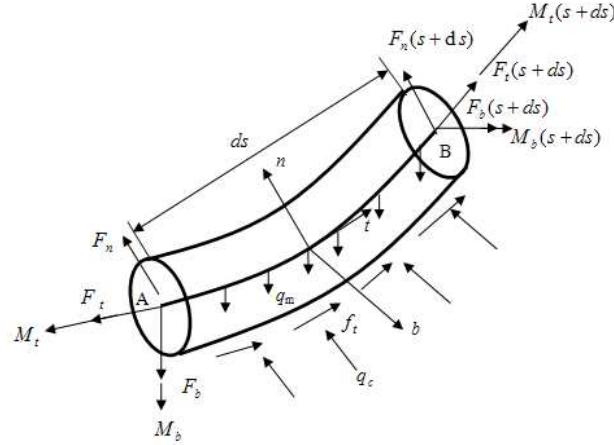


Fig.1 String stress analysis

Tension-torque differential equations is

$$\left. \begin{aligned} \frac{dT}{ds} + K \frac{dM_b}{ds} \pm \mu_a(N + \Delta N) - q_m K_f \cos \alpha &= 0 \\ \frac{dM_t}{ds} &= \mu_r R(N + \Delta N) + \Delta M_t \\ \frac{d^2 M_b}{ds^2} - K \cdot T - N_n + q_m K_f \cos \alpha \frac{K_\alpha}{K} &= 0 \\ K \frac{dM_b}{ds} - N_b + q_m K_f \sin^2 \alpha \frac{K_\phi}{K} &= 0 \end{aligned} \right\} \quad (1)$$

Where: T is axial tension; M_b is bending moment, $N \cdot m$; K is dog-leg of well hole, rad/m ; E is elasticity modulus of steel, Pa ; μ_a is axial friction coefficient; μ_r is circumferential friction coefficient; q_m is a weight per unit length, kg/m ; K_f is buoyancy coefficient; α is deviation angle, rad ; K_α is deviation rate, rad/m ; K_ϕ is azimuth rate, rad/m ; k_b is borehole curvature; k_n is borehole torsion; M_t is torque, $N \cdot m$; N_b is the pressure in the direction of e_b , N ; N_n is the pressure in the direction of e_n , $N \cdot m$; N is positive pressure, N ; ΔN is additional pressure for column buckling; R is string radius, m ; ΔM_t torque produced by buckling, $N \cdot m$; $N^2 = N_n^2 + N_b^2$.

The drill string sine buckling caused by compression, sine buckling doesn't consider additional torque, the drill string and between the wall of the lateral force should also be added by the drill string sine buckling and of generation contact force

$$\Delta N = \frac{rT^2}{8EI} \quad (2)$$

The drill string spiral buckling pressure happens; the string and the wall of the lateral force should also be additional drilling column by spiral buckling and of generation contact force

$$\Delta N = \frac{rT^2}{4EI}; \Delta M_t = -\mu_t R \frac{r^2 T^2}{4EI} \sqrt{\frac{-T}{2EI}} \quad (3)$$

Where: I is moment of inertia section, m^4 ; r is radius difference between wellbore and string, m .

2 Horizontal well buckling string stress analysis and strength check

The stress of buckling string for an extended reach well includes: bending stress caused by bending; circumferential stress and radial stress caused by internal and external pressure; shearing stress; axial stress caused by axial tension, temperature and spiral buckling.

(1) Bending stress

Mechanical analysis can prove: bending stress is larger in borehole curvature changes greatly, namely slant drilling section; the surface of string is the danger point ($r' = r_o$). In this area, bending stress is caused by borehole bending and drill strings bending moment

$$\sigma_b = Ek_b r + \frac{4M_w r'}{\pi(r_o^4 - r_i^4)}. \quad (4)$$

Where: M_w is Bending moment, N·m; r' ($r_i \leq r' \leq r_o$) is the distance from bending point to neutral axis, m.

(2) Circumferential stress and radial stress

$$\sigma_r = \frac{p_i r_i^2 - p_o r_o^2}{r_o^2 - r_i^2} - \frac{(p_i - p_o) r_o^2 r_i^2}{(r_o^2 - r_i^2) r^2}; \sigma_\theta = \frac{p_i r_i^2 - p_o r_o^2}{r_o^2 - r_i^2} + \frac{(p_i - p_o) r_o^2 r_i^2}{(r_o^2 - r_i^2) r^2}. \quad (5)$$

Where: σ_r is radial stress, Pa; σ_θ is circumferential stress, Pa; r_i is string inner diameter, m; r_o is string outer diameter, m; r ($r_i \leq r \leq r_o$) is radial coordinate, m; p_i p_o are respectively internal pressure and external pressure.

(3) Shearing stress

$$\tau_m = \frac{4M_t r'}{\pi(r_o^4 - r_i^4)}. \quad (6)$$

(4) Axial stress caused by axial tension, temperature and spiral buckling

$$\sigma_t = \frac{T}{A} + E \cdot \left(\sqrt{1 + \frac{r^2 T}{2EI}} - 1 \right) + \alpha \Delta T; A = \pi(d_o^2 - d_i^2)/4. \quad (7)$$

Where: σ_t is axial stress, Pa; A is cross-sectional area of string, m².

(5) Equivalent stress

$$\sigma_{tb \max} = \sigma_t + \sigma_b; \sigma_{tb \min} = \sigma_t - \sigma_b. \quad (8)$$

Where: $\sigma_{tb \max}$ $\sigma_{tb \min}$ is respectively maximum and minimum equivalent axial stress, Pa.

Equivalent stress can be calculated by the fourth strength theory

$$\sigma_{eqv} = \sqrt{\sigma_{tb}^2 + \sigma_r^2 + \sigma_\theta^2 - (\sigma_{tb}\sigma_r + \sigma_r\sigma_\theta + \sigma_\theta\sigma_{tb}) + 3\tau^2} \leq [\sigma]. \quad (9)$$

Where: σ_{eqv} is equivalent stress, Pa; $[\sigma]$ is allowable stress, Pa.

Mean stress and stress amplitude are respectively

$$\sigma_m = \frac{1}{2}(\sigma_{eqv \max} + \sigma_{eqv \min}); \sigma_a = \frac{1}{2}(\sigma_{eqv \max} - \sigma_{eqv \min}). \quad (10)$$

Where: σ_m is mean stress, Pa; σ_a is stress amplitude, Pa.

3 Horizontal well buckling string life prediction models

The crack in component usually has three types: open type, slid open type, tearing his type. Through testing the used of the string, most of the surfaces of the drill string have across-sectional and longitudinal scratches. The type of geometric shape factor of scratch belongs to linear crack^[8].

$$F_m = 1 + 0.128(a_L/D_0) - 0.288(a_L/D_0)^2 + 1.525(a_L/D_0)^3. \quad (11)$$

Where: a_L is half long of linear cracks, m; D_0 is drill string average diameter, m.

The main reason of fatigue damage is that the process of using and manufactures the drill string. In certain conditions of using, initial crack will appear and expand. The change of stress intensity factor, the critical crack dimensions and fatigue life as follows

$$\left. \begin{aligned} \Delta K = F_m \Delta \sigma \sqrt{\pi a}; \alpha_c = \frac{K_{IC}^2}{F_m^2 \sigma_m^2 \pi}; R = \frac{\sigma_{eqv \max}}{\sigma_{eqv \min}} \\ N = \frac{(1-R) K_{IC}}{c (\Delta \sigma F_m \sqrt{\pi})^n} \left(\frac{a_c^{1-\frac{n}{2}} - a_0^{1-\frac{n}{2}}}{1-\frac{n}{2}} \right) - \frac{1}{c (\Delta \sigma F_m \sqrt{\pi})^{n-1}} \left(\frac{a_c^{1-\frac{n-1}{2}} - a_0^{1-\frac{n-1}{2}}}{1-\frac{n-1}{2}} \right) \end{aligned} \right\} \quad (12)$$

Where: da/dN is crack propagation velocity; a is crack length, m; N is stress cycling times; ΔK is variations of stress intensity factor, $\text{MPa}\sqrt{\text{m}}$; K_{IC} is fracture toughness, $\text{MPa}\sqrt{\text{m}}$; R is stress ratio; c, n are material constants.

4 Examples

It is a horizontal well in Jilin oilfield. The data includes: the well measured data of inclined in Fig. 2, down hole assembly in table 1, and the well deep structure in table 2. drilling fluid density is 1078 kg/m^3 , surface temperature 11°C , geothermal gradient $2.3^\circ\text{C}/100 \text{ m}$, the danger point in inclined section or a serious dogs leg hole section, well depth is 1130m, torque is $T=15316.7 \text{ N}\cdot\text{m}$, hook load $F=263.441\text{kN}$, drilling pressure $p=133.4\text{kN}$, standpipe pressure $p_0=10\text{MPa}$, well diameter $D_w=215.9\text{mm}$, drilling rate $n_r=100\text{r/min}$, $E=2.06\times 10^{11} \text{ Pa}$, $a_L=0.5\text{mm}$, material constants $n=1.07$, $c=6.14\times 10^{-14}$, fracture toughness $K_{IC}=98.9 \text{ MPa}\sqrt{\text{m}}$.

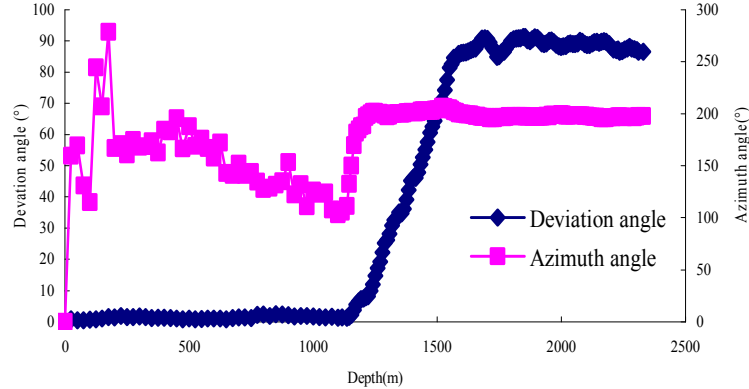


Fig.2 Inclination data

Table 1 Bottom hole assembly

Drill type	Length(m)	Outer diameter (m)	Inner diameter (m)	Unit Weight(kg)
Bit	0.305	250.83	82.55	387.31
Stabilizer	1.524	158.75	50.8	229.71
Mud Motor	9.144	203.2	63.5	229.71
Drill collar	9.449	196.85	57.15	214.05
Stabilizer	1.524	158.75	50.8	229.71
Drill collar	9.449	196.85	57.15	214.05
Stabilizer	1.524	158.75	50.8	229.71
Drill collar	82.296	196.85	57.15	214.05
Heavy pipe	283.464	127	76.2	73.37
Drill pipe	1931.321	127	108.6	31.09

Table 2 Casing programme

Casing programme	Top MD (m)	Down MD (m)	Outer diameter (m)	Inner diameter (m)	Friction coefficient
Surface casing	0	152.4	609.6	482.6	0.2
intermediate casing	152.4	1706.88	311.15	258.88	0.2
Open hole	1706.88	2330	253.36	—	0.25

The rotating drill string fatigue life prediction rules curve show as Fig.3 and Fig.4.

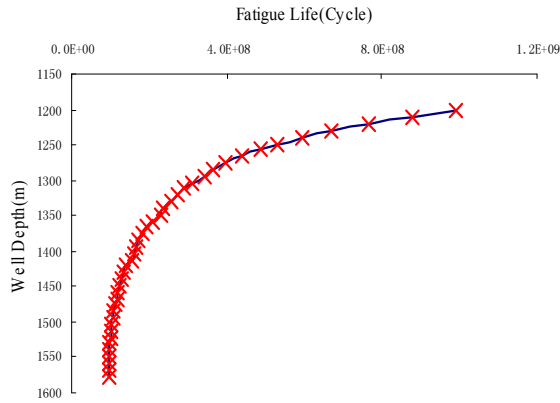


Fig.3 Rotating drill string fatigue life prediction rules curve in building section

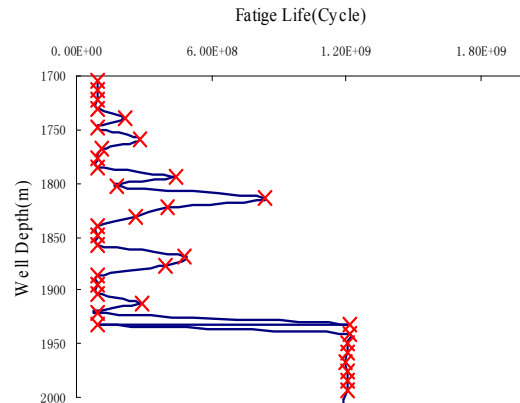


Fig.4 Rotating drill fatigue life prediction rules curve in horizontal section

Conclusions

- (1) Rotating drill string underground and tension, pressure, curved, temperature and so on many kinds of loads, however, the main reason is that rotating drill string of fatigue failure is comprehensive effects of alternating stress.
- (2) Fatigue life prediction of rotating drill string with initial crack is common in the field conditions. Therefore, studying the fatigue failure mechanism and the fatigue life prediction is a good reference to both operation and monitor of the drill pipe.
- (3) The rules curves of rotating drill string fatigue life prediction illustrate that borehole curvature and buckling have an important effect on rotating drill string fatigue life, prediction results of the model agree with field use, which has great important significance for application to field.

Acknowledgements

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Analysis on the Influence Factors of Well Deviation in Gas Drilling

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Keywords: gas drilling; well deviation; stress difference; rock breaking mechanism; borehole enlargement

Abstract. Well deviation control has become a bottleneck restraining the development of gas drilling. Without lubrication of drilling fluid and the existence of negative pressure differential, the reasons of well deviation in gas drilling are different from in mud drilling. The effects of stress distribution difference, rock-breaking mechanism, well bore enlargement and water export on well deviation during both gas drilling and mud drilling are compared and studied on the basis of the previous studies in this paper. The conclusion demonstrates that the new stress state of the bottom rock, the uneven crater which is formed by rock breaking and the borehole enlargement are the main causes of well deviation during gas drilling.

Introduction

Gas drilling has been successfully applied in many oil fields for its remarkable predominance in increase the rate of penetration, decrease formation damage, drill lost-circulation formation and low-permeability reservoir. However, problems such as well deviation, water export, borehole instability, well control and other accidents may appear in gas drilling, which restrain the development of gas drilling. Well deviation control has become a bottleneck.

For mud drilling, the mainly influence factors of well deviation can be divided into two types of geological factors and drill factors. Geological factors include formation anisotropy, formation dip angle, layer structure, fault and so on. Drill factors mean drill bit tilt because of tool inclination and flexion, resulting in asymmetric cutting in bottom hole. The bit subjected to a lateral force and cut lateral, well deviation is easy to take place. For gas drilling, formation factors on the influence of well deflection are not change, but the degree change with different situations. Without lubrication of drilling fluid, working environment and status of BHA have changed, resulting in the distortion and force have a great change. And the existence of negative pressure differential causes a considerable reduction in the rock strength; rock breaking efficiency and penetration rate are increased obviously. The condition for fast growth of well deviation is formed. It is necessary that we work deep in the research of influence factors to control well deviation in gas drilling effectively.

Many scholars at home and abroad have studied gas drilling deviation control from bottom-hole pressure differential [1], formation dip angle [2,3], and the mechanics characteristics of BHA[4]. Some valuable conclusions are drawn [5,6,7]. Based on previous study, combine the actual conditions of Daqing Oilfield, the impact of the distribution of rock stresses, the mechanism of rock fragmentation, and well hole enlargement on well deviation in gas drilling are analyzed in this paper.

1 Statistical analysis of gas drilling well deviation

Practical drilling data of ten gas drilling wells in Daqing Oilfield is collected. According to wellbore quality requirement, six wells within the range of deviation angle. Four wells beyond. The data is illustrated in Fig.1 and Fig.2.

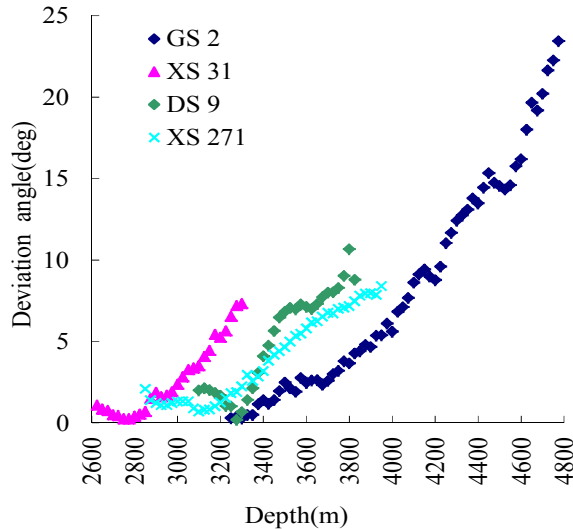


Fig. 1 Well Deviation Trend Chart

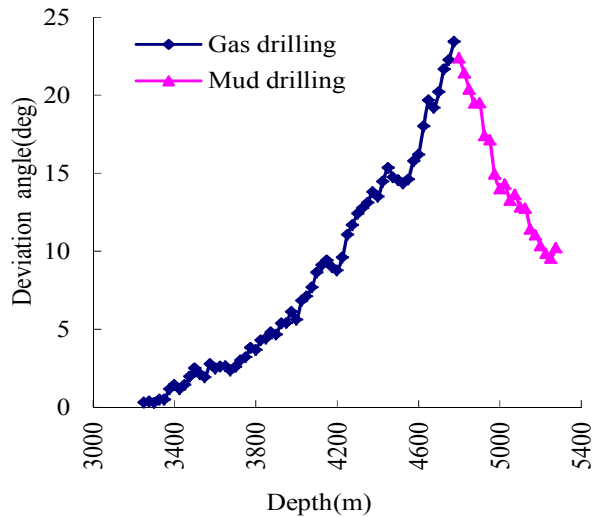


Fig. 2 Well Deviation Contrast Map between Gas Drilling and Mud Drilling

As seen in Fig.1, well inclination increased by 5.4° when 745m is drilled with NUMA air hammer while 17° is increased when 776m is drilled using cone bit and packed hole assembly in GS 2. Well inclination grew by 6.7° when packed hole assembly drilling 579m in XS 31 as 7.6° of 793m in XS 271. The reason is packed hole assembly can not drop angle as well deflects. And ROP is high in air drilling, i.e., 4-5 time as high as that of mud drilling, resulting in fast growth of hole angle. When slick collar assembly is used under light WOB ($<20\text{KN}$) to drill 700m, well deviation rose nearly 9° in DS 9. This is because bit move forward along formation dip direction due to the particularity of air drilling, well inclination grow fast.

As seen in Fig.2, hole angle drop rapidly when gas drilling switch to mud drilling.

In conclusion, hole inclination in air drilling develops quickly with a large dogleg severity ascribing to fast ROP. And its control is much difficult.

2 Comparative analysis of well deviation mechanism

In mud drilling, researches focus on formation anisotropy, and the result is also quite simple. In gas drilling, a heavy deformation of BHA is formed caused by the difference of circulating medium. The stress state of rock and breakage properties present a big variation due to the alteration of bottom hole peripheral pressure. Therefore, there is a big difference for deviation mechanism in mud drilling and in air drilling.

(1) Influence of the changes of circumferential stress and bottom hole stress

The stress condition of rock both on the wall and on the bottom takes a radically alteration in gas drilling leading to the change of stratum anisotropy. Bit straight ahead in the direction of rock broken easily. The bit stability is not very good. Thus, the borehole is prone to deviation and azimuth is uncertain.

1) Influence of circumferential stress

With same rock mechanics parameters, the deformations of rock on the wall both in gas drilling and mud drilling are shown in Fig.3 and Fig.4.

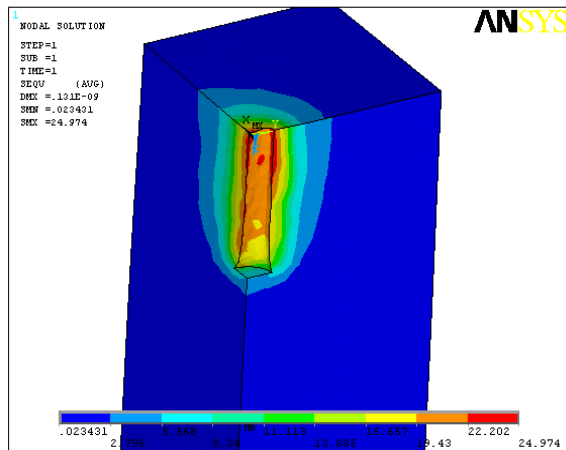


Fig.3 Von Mises Stress in Mud Drilling

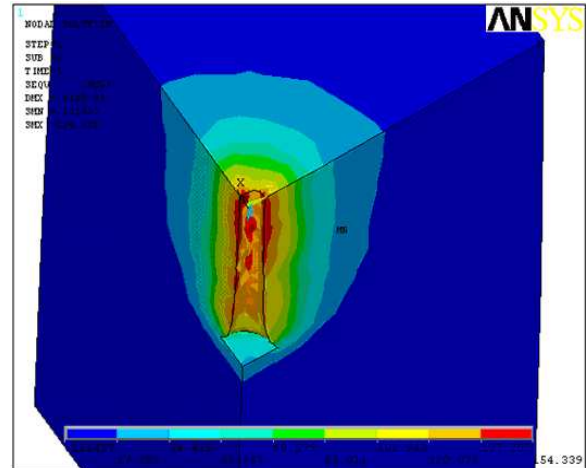


Fig.4 Von Mises Stress in Gas Drilling

The conclusions as follows:

- Under unequal horizontal stress, tensile stress is larger on higher-stress side both in gas drilling and in mud drilling. The bit first break rock in this direction, if assumed that bit is isotropy. The tendency of hole angle drift to the orientation of the maximum horizontal principal stress.
- With the same formation conditions, the stress distributed regularly in mud drilling. Stress concentration regions mainly in the middle of the maximum horizontal principal stress and the minimum horizontal principal stress. However, the stress distribution around well bore is mostly irregular in gas drilling. And the area of stress concentration is larger than in mud drilling. Two tensile stress concentration regions are located in the middle of the maximum horizontal principal stress and the minimum horizontal principal stress. Rock in these areas is easily broken. Therefore, hole is easy to deviate during rock-breaking process.
- The difference value between the maximum horizontal principal stress and the minimum horizontal principal stress in mud drilling is smaller than of in gas drilling. Formation anisotropic index is larger in gas drilling than that of in mud drilling and formation natural deflecting force increase accordingly. That explains the reason why the hole is apt to deviation in air drilling.

According to the analysis, it is found that formation anisotropic index is magnified because of non-uniformity of the circumferential stresses which manifests a great hole deviation tendency in air drilling.

2) Influence of bottom hole stress

The stress under bottom shows as tensile stress whereas stress shows as compression stress in mud drilling. The stress distributed regularly in the direction of the minimum principal stress. The bit does not deflect when break rock in this region. Tensile stress is maximal in the direction of the maximum principal stress as shown in Fig.5. From the stress state of bottom hole, the difference of stress is 49MPa. Rock is liable to break under shear and impulse impact because of small compression stress which is caused by the existence of tensile stress. ROP is high in this direction and hole tilt toward the same direction.

The difference of stress in bottom hole is large as a result of negative pressure. Formation anisotropic index in air drilling is larger than that of in mud drilling and formation natural deflecting force increase accordingly which indicates hole is easy to deviate.

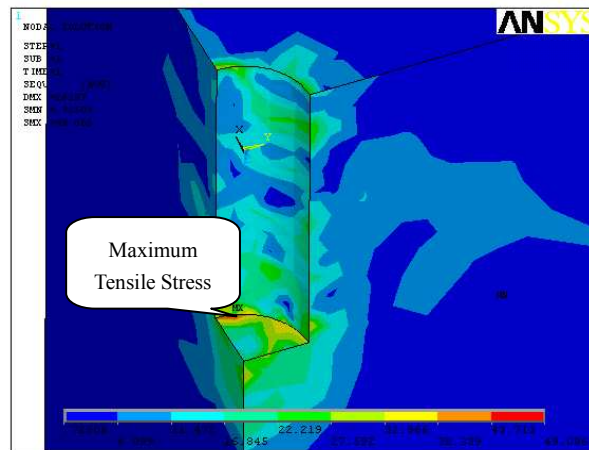


Fig.5 Von Mises Stress of Borehole in Gas Drilling

(2) Influence of rock breaking mechanism

In mud drilling, the rock-breaking mechanism of roller bit teeth is the theory of push, shear and slip. The process can be described as five stages: surface micro broken stage, elastic deformation stage, viscous deformation stage, micro-crack initiation and development stage, brittle broken stage.

Rock breaking form in gas drilling is different from in conventional mud drilling. The stress state of bottom hole is changed by nearly weightless gas column, as shown in Fig.6 and Fig.7. The bottom rock is unloading damaged with overburden pressure gradually unloading. The rock-breaking mechanism is the theory of internal energy release and rock blasting which means bottom rock escape the chip hold down effect and release the internal energy caused by the accumulation of overburden pressure to break rock. The process can be described as five stages: internal energy accumulation and expansion stage, micro-crack initiation stage, crack extension stage, crack brittle crush stage and shear breakage stage.

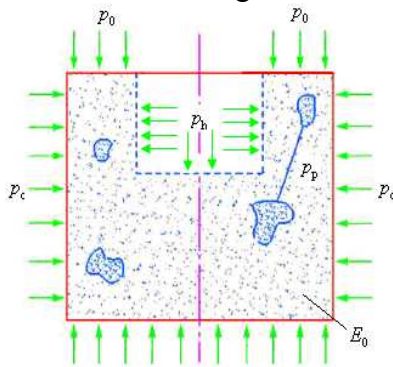


Fig.6 Stress of Wellbore in mud Drilling

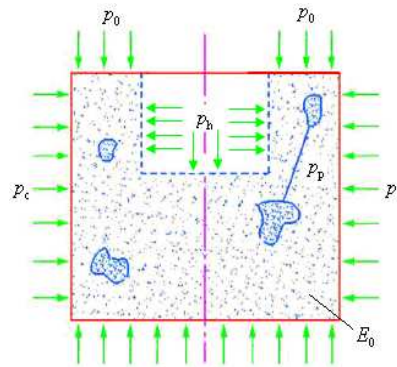


Fig.7 Stress of Wellbore in gas Drilling

The crushed rock volume is different due to the different lithology and hardness of rock when drill certain angle formation. Soft brittle rocks generate large carter. And the bit slip into larger carter under transverse force owing to WOB which indicate hole inclination develops quickly, as shown in Fig.8.

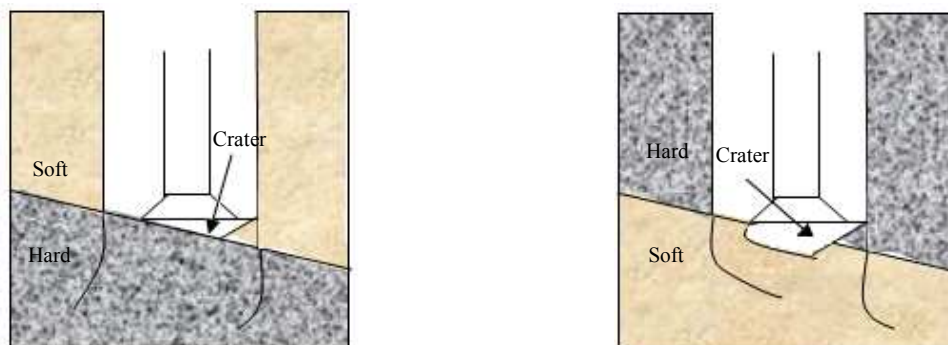


Fig.8 Carter of Different Rocks in Gas Drilling

(3) Influence of borehole enlargement

The unallowable wellbore enlargement rate is the common serious problem in gas drilling, as shown in Fig.9. Well hole enlargement induce variation of BHA stress state. Bit side force increased with low tangential point and heavy unit weight which causes well deviation. Cuttings cushion is formed with the results of particles detached which affect the mechanical properties of BHA. Buildup force is occurred and hole deviation develop.

In general, hole enlargement not easily resulted in well deviation under low WOB while well deviation is easily produced under high WOB, as shown in Fig.10. Borehole enlargement is the significant cause of well deviation during gas drilling under high WOB.

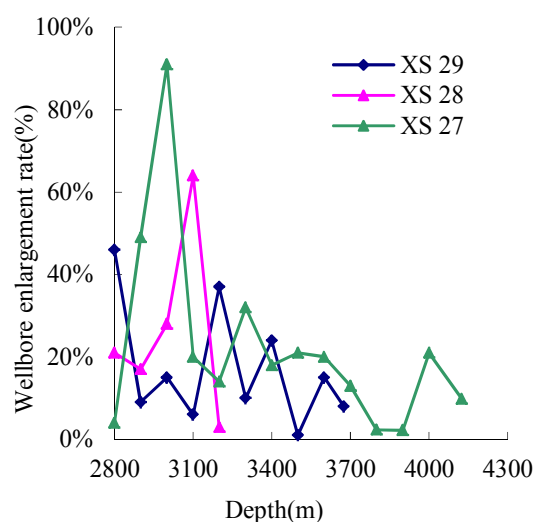


Fig.9 Borehole Enlargement in Gas Drilling

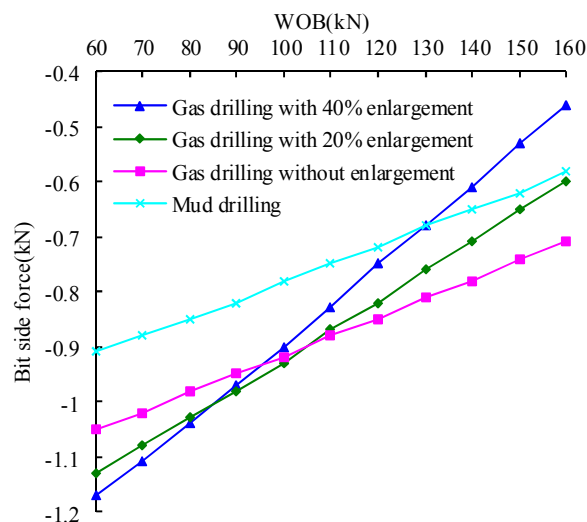


Fig.10 Comparison of Bit Side Force with Different Enlargement Rate

Conclusions

(1) The stress state of rock both on the wall and on the bottom in gas drilling takes a radically alteration. Formation anisotropic index is greatly larger than that of in mud drilling which obviously increase formation deflecting force. That is the main reason why the borehole is prone to deviation and the control is difficulty.

(2) The rock breaking is brittle explosion in gas drilling, different crushed rock volumes induce the bit slip into the bigger crater which increase the tendency of deviation building up.

(3) Borehole enlargement is the significant cause of well deviation during gas drilling under high WOB.

Acknowledgements

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Research and Application of Technical Pipe String with Integrating Layered Gas Production in Oil Production Engineering of Mining Engineering

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Keywords: Integrating eccentric gas distributor; Gas production by layer; Interlayer interference; Recovery

Abstract. In oil production engineering, layered gas production is an important mining technology. While the interlayer pressure of natural gas well differs big, the interlayer interference forms. It is difficult to exploit the low pressure layer and control the high pressure layer. Developing a technical pipe string with integrating layered gas production can solve the above problems. This technical pipe string changes throttling area by striking, solves the conflicts between each layer, mines each layer uniformly and enhances recovery. It applied to Tai 4-28 gas well in Sebei-gas-field which is located in east of Qaidam basin perfects the 4th department of shallow layer well pattern, forms new capacity, controls each layer pressure and capacity smoothly, protects the reservoirs effectively, achieves good effect in practice.

Introduction

In the process of exploiting natural gas well, the interlayer pressure is generally nonuniform. While the pressure differs big, the interlayer interference forms if the conventional mixed exploiting method is used [1]. It becomes difficult to exploit the low pressure layer and control the high pressure layer, so the capacity of each layer is affected. In addition, the difficulty of impurity separation and purification will be increased and the amount of natural gas will be affected [2] while the component of each layer differs. Gas production by layer needs to solve the interlayer conflicts, enhance recovery and reduce the difficulty of gas treatment.

Integrating layered gas production technical pipe string which adopts integral governing technique and changes throttling area by striking is applicable to exploit gas by layer and developed in China for the first time. It can solve the interlayer interference and conflicts effectively and control the capacity of each layer. Compared to dual string gas production technique, it avoids the excess of cost using just one group of pipelines; it improves the safety of filed operation because the gas distributor can reduce and control the pressure underground which makes the natural gas into the pipeline stay steady state; it saves building the surface reducing pressure and measuring system in the ground because the capacity is measured underground directly and correctly. Compared to conventional mixed exploiting method, it saves cost because the integral governing air tap in the integrating eccentric gas distributor avoids changing varisized air tap by throwing-in and pulling operation; it avoids easily happened tap broken phenomenon and sand production conduced steel wire broken problem in the process of throwing-in and pulling operation.

Structure and Working Principle

Structure and working principle of integrating layered gas production technical pipe string. The structure of integrating layered gas production technical pipe string is shown in Fig.1. This pipe string is composed of draw-tube, Y441-148 packer, anti-sand mechanism, JF-114 integrating eccentric gas distributor, Y341-148 packer and extension pipe.

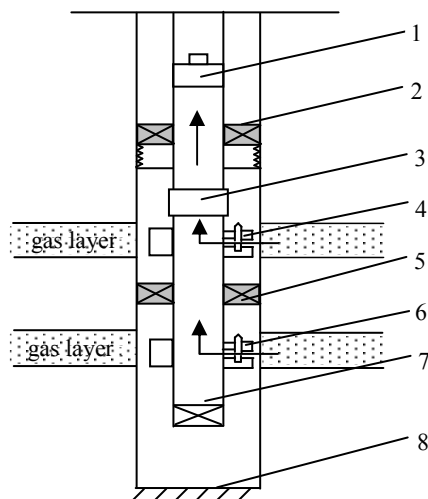


Fig.1 The Schematic Diagram of Integrating Layered Gas Production Technical Pipe String

1—draw-tube; 2—Y441-148 packer; 3—anti-sand mechanism; 4, 6—JF-114 integrating eccentric gas distributor; 5—Y341-148 packer; 7—extension pipe; 8—artificial bottom hole.

Technical parameters of the integrating layered gas production technical pipe string are shown in Table 1 to 4.

Table 1 The Technical Parameters of Packers

Component	Y441-148 packer	Y341-148 packer
Technical parameters		
Total length(mm)	1200	1200
Maximum external diameter(mm)	148	148
Minimum internal path(mm)	62	62
Setting pressure(MPa)	14	14
Releasing power(kN)	35	35
Stand pressure difference(MPa)	30	20
Ppper and lower joint thread	2 ⁷ / ₈ TBG	2 ⁷ / ₈ TBG

Table 2 The Technical Parameters of Integrating Eccentric Gas Distributor

External diameter(mm)	114
Total length(mm)	1400
Internal path(mm)	46
Adjustable air tap diameter(mm)	0~16
Upper and lower joint thread	2 ⁷ / ₈ TBG

Table 3 The Technical Parameters of Draw-tube

External diameter (mm)	140
Internal path (mm)	62
Total length (mm)	1800
Upper and lower joint thread	2 ⁷ / ₈ TBG

Table 4 The Technical Parameters of Anti-sand Mechanism

External diameter(mm)	110
Total length(mm)	600
Safety tonnage(kN)	<200
Upper and lower joint thread	2 7/8 TBG

The core and great advantage of this pipe string is developing the integrating eccentric gas distributor. Convert the throwing-in part of the throwing-in and pulling mechanism which is used in conventional mixed exploiting method to striker, and then the sector annulus area can be changed randomly without throwing-in and pulling taps. Then it achieves production allocation results for different layers and controls production pressure for each layer effectively. So it achieves improving individual well production and recovery. It can be put into multiple-stage operation. According to well conditions, the stage is not restricted. One stage increased one integrating eccentric gas distributor and one Y341-148 packer is added.

Setting and releasing principle of integrating layered gas production technical pipe string.

The packer in the integrating layered gas production technical pipe string is composed of setting mechanism, sealing mechanism, retaining mechanism and releasing mechanism. The setting principle is injecting pressure to hydraulic cylinder attached to setting mechanism, then the pressure is transmitted to the packer rubber [3]. The packer rubber is compressed and deformed in radial direction, so the tubing-casing annular space is sealed. At the same time, retaining mechanism is locked automatically and the compressed displacement is retained, which makes the packer rubber can not reset [4]. Thus, the packer is set. When release the packer, lift the string pipe then the top connection drives the central tube move up, the external central tube keep still as the friction between the packer rubber and casing [5]. While the lifting power reaches rated tonnage, the shear pin is cut, then the rubber and the other part of the packer and is reset. So the releasing process is complicated.

JF-114 integrating eccentric gas distributor. JF-114 integrating eccentric gas distributor is the core of the string pipe. It is composed of et mandrel and integrating blanking plug.

There are two via holes in the et mandrel. One is concentric with pipeline through which the other technology can be operated successfully. The other one is a eccentric via hole which is connected with blanking plug. The top clip spring of the blanking plug pops by virtue of reducing nipple and pushes the blanking plug into the eccentric via hole when it enters the eccentric via hole.

The integrating blanking plug is composed of throwing-in and pulling mechanism, spring, clip spring, track mechanism, gear, sealing mechanism and tap. There are two functions of throwing-in and pulling mechanism: one is ensuring the throwing-in and pulling operation of blanking plug; the other is receiving striking. Clip spring is the mechanism which connects and fixes the blanking plug and et mandrel. Spring, track, gear and tap form a integrating mechanical stroke mechanism.

The principle of JF-114 integrating eccentric gas distributor changes the relative point location between the stationary element and the motional element attached to integral mechanism by striking. Once striking, the motional element rotates 30° relatively and the flow area changes. The range of angle is $[0, 2\pi]$. Set the throttling area S , $S=f(\theta)$, the diameter of stationary element D , the diameter of motional element d , the included angle between stationary element and motional element θ , the included angle between stationary element and motional element after striking α , then

$$df(\theta) = \frac{\pi(D^2 - d^2)}{360} \cdot d\theta \quad (1)$$

Integrate the left and right sides of equation (1) simultaneously, then

$$S = f(\theta) = \int_0^\alpha \frac{\pi(D^2 - d^2)}{360} d\theta = \frac{\pi(D^2 - d^2)}{360} \theta \Big|_0^\alpha, \quad \alpha = \frac{n\pi}{6}, n = 0, 1, 2, \dots, 11 \quad (2)$$

During the gas exploiting process, the throttling area of each layer needs to be calculating according to the set capacity of each layer and then the number of each integrating eccentric gas distributor stroke is known. After striking, the natural gas of each layer comes into the eccentric via hole through the internal via hole of the et mandrel. Then, the gas is produced ground after the integrating blanking plug throttled. In addition, the sealing mechanism ensures the gas flow as the designed direction and come out to the ground finally.

Layered gas principle of integrating layered gas production technical pipe string. The integrating layered gas production technical pipe string can be put into multiple-stage operation. Taking two gas layers for example, the pipe string works as follows: join the pipeline and put it into the set position downhole, inject pressure to the pipeline. While the pressure reaches 21MPa, the packers are set and the two layers are separated completely and then the gas can be exploited. The size of the tap attached to integrating eccentric gas distributor can be set in the ground before the pipeline thrown into the well, and also can be set downhole after the pipeline thrown into the well.

If the tap size set in the ground is unsuitable or it needs adjusting through a period of production time during which the interlayer pressure changes, the adjusting operation can be easily realized downhole. If both the capacity of two layers need to be adjust, adjust the bottom tap first and then the top. As shown in Fig. 1, the method of setting or adjusting the bottom tap is like this: throw the throwing-in and pulling mechanism through the pipeline to the position of the bottom eccentric gas distributor 6 and then change the size of the tap by striking the blanking plug attached to gas distributor 6. When the striking number reaches the designed number, lift the throwing-in and pulling mechanism to the position of the top eccentric gas distributor 4. The method of setting or adjusting the top tap is striking the blanking plug attached to gas distributor 4. When the striking number reaches the designed number, lift the throwing-in and pulling mechanism to the ground. If only one layer capacity needs to be adjusted, use to above method to adjust the size of corresponding tap.

Application of Integrating Layered Gas Technology

Application of integrating layered gas production technical pipe string has been put into a new geology project of Tai 4-28 gas well in Sebei-gas-field which is located in east of Qaidam basin. The basic data and the layer condition are shown in Table5 and Table6.

Table 5 Basic Data of Tai 4-28 Gas Well

1. Structural location: in the 80°direction and 289 meters away from Tai 6-5 well in the eastern structure in Qaidam basin		
2. Well numbers: Tai 4-28 gas well	Well type: development well	
3. Well coordinate: X=4140714.9	Y=16566833.1 (Beijing coordinate system, preliminary survey)	
4. Ground elevation: 2690.66m	bushing elevation: 2698.16m	
5. Total depth: 1515.00m	hindered position: 1501.15m	
6. Surface section time: 12:00 July 4th, 2009 Drilling finish time: 17:00 July 12th, 2009	Second section time: 13:30 July 6th, 2009 Well completion time: 10:00 July 17th, 2009	
7. Artificial bottom hole : 1501.15m	Cementing quality: qualified	
8. Short casing position: 1) 1260.17m-1263.70m,	3.53 m long;	
2) 1019.25m-1022.78m,	3.53 m long;	
9. Maximum inclination: 1.50°;	Direction: 171.52°;	Well depth: 175.00m

Table 6 Perforation Data of Tai 4-28 Gas Well

Stratigraphic exploration	Stratigraphic group	Layer number	Perforated Interval(m)	Thickness/effective thickness (m)	Hole density (hole number/m)	Hole number(hole)	Layer
IV	IV-3	3-1-1	1439.3-1441.0	1.7/1.7	24	41	I
		3-1-2	1442.9-1444.5	1.6/1.6	24	38	II
		Total		3.3/3.3		79	

Effect of application. Tai 4-28 gas well in Sebei-gas-field which is located in east of Qaidam basin is a new production well, the interlayer pressure differs big and so the interlayer interference. The average pressure of layer 3-1-1 is 41.2MPa and the average pressure of layer 3-1-2 is 19.8MPa. So the interlayer pressure is 21.4MPa. It is difficult to exploit the low pressure layer and control the high pressure layer if the gas layered method is not adopted. Even the high pressure layer will pour into the low pressure layer which destroys reservoir. Putting the integrating layered gas production technical pipe string into application to exploit gas perfects the 4th department of shallow layer well pattern, forms new capacity, allocation reaches 52000m³/d which satisfies the user's demand. The pressure and capacity keeps stable and workover job has never been taken nearly a year since the gas production started. So the gas layered production goal is achieved.

Conclusions

The integrating layered gas production technical pipe string sets stably and changes the sector annulus area randomly without throwing-in and pulling tap. It is applicable to exploit gas by layer and developed in China for the first time. It can solve the interlayer interference and conflicts effectively and control the capacity of each layer, especially for the new gas well or the high interlayer pressure gas well.

Compared to dual string gas production technique, it avoids the excess of cost, improves the safety of filed operation and saves building the surface reducing pressure and measuring process. Compared to conventional mixed exploiting method, it saves cost because it avoids the easily happened tap broken phenomenon and sand production conducted steel wire broken problem in the process of throwing-in and pulling operation.

The application of this technology has been put into Tai 4-28 gas well in Sebei-gas-field which is located in east of Qaidam basin. It develops the low pressure layer successfully and controls the high pressure layer smoothly, reserves the reservoir effectively, avoids high pressure layer pouring into low pressure layer phenomenon which destroys the reservoir. It perfects the 4th department of shallow layer well pattern, forms new capacity and the pressure and capacity keeps stable and workover job has never been taken so far.

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Development and Research on Multi-functional Sucker-rod Pump Lifting Simulation Experiment System in Oil Mining Engineering

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Keywords: Sucker-rod pump; Multifunctional; Simulation experiment; Submergence depth; Displacement coefficient

Abstract. In oil mining engineering, oil production technology becomes more and more complicated while the oilfield production steps into the middle-later development time, meanwhile, its matching lifting technology becomes more and more complicated and diversified. So the demand of intermediate experiment for lifting technology in petroleum industry becomes more and more obvious. It is necessary to develop a sucker-rod pump lifting simulation experiment system in the lab which can simulate practical work. The developed system can provide reliable experiment data for evaluating sucker-rod pump technical properties and developing new sucker-rod pump. It is benefit to innovate and promote the development of sucker-rod pump lifting technology.

Introduction

The properties of sucker-rod pump influence the oilfield capacity and economic benefit directly as important oilfield lifting device. The oil extraction technology becomes complicated and the matching lifting technology becomes diversified gradually while the oilfield extraction steps into the middle-later period. But there is less laboratory evaluation experiment device or ways for lifting technology while the demand becomes more and more obvious.

From 1990 to 1994, Daqing Petroleum Institute developed "deep well pump-pumping unit experiment device"[1]; Oil Production Technology Institute of Shengli Oilfield and Petroleum University jointly developed "horizontal well sucker-rod pump simulation experiment device" in 1995; Southwest Petroleum Institute developed "horizontal well(controlled directional well) sucker-rod pump experiment system"[2] in 1997; Petroleum University(Beijing) developed a gas-liquid two-phase flow sucker-rod pump experiment device[3] in 1999; Daqing Oilfield and Daqing Petroleum Institute jointly developed "sucker-rod pump lifting simulation experiment system" in 2007[4]. All the above experiment devices belong to simple and single functional devices of which the parameters regulation range is limited. They are no longer suitable for lifting technology development nowadays. So it is quite necessary to develop a sucker-rod pump lifting simulation experiment system in the lab which is suitable for practical oilfield production.

System Function and Technical Index

In order to develop a adaptable experiment device which can provide intermediate platform and method for lifting technology and lifting device, improve the properties of sucker-rod pumps as well as reduce development period and enhance field experiment effect, the multi-functional sucker-rod pump lifting simulation experiment system should have the following functions:

1. It can simulate the working state of the sucker-rod pump under certain lift height and submergence depth in dip range $0\sim 90^\circ$.
2. It can test the hydraulic property parameters of the sucker-rod pump.
3. It can simulate gas-bearing, adding sand and other different working state; test various corresponding hydraulic property parameters at the same time.
4. It can complete special type sucker-rod pump parameter property experiment.
5. It can carry out 38 mm oil well pump to 140 mm oil well pump experiments which cover field application range at present.

The technical parameters of the multi-functional sucker-rod pump lifting simulation experiment system are shown as follows:

1. Dip range is $0\sim 90^\circ$. Every 10° is a grade and it is adjustable by grade.
2. The stroke is stepless adjustable and its maximum is 5m.
3. The stroke number is stepless adjustable and its maximum is 6 min^{-1} .

While the stroke is 5m, the set stroke number of 140 mm oil well pump should be set less than 2 min^{-1} , 3 min^{-1} for 120 mm oil well pump and 5 min^{-1} for 95 mm oil well pump.

4. The temperature range of test medium is room temperature $\sim 90^\circ\text{C}$.
5. The sucker-rod pump inlet submergence pressure range is $0\sim 3\text{ MPa}$.
6. The sucker-rod pump outlet pressure range is $0\sim 15\text{ MPa}$.
7. The polished rod load is less than 120kN (12t).
8. The max instantaneous flow is less than $500\text{ m}^3/\text{d}$.
9. The adding gas flow is less than $1\text{ m}^3/\text{min}$ (converting the value at standard atmospheric pressure).
10. The max adding sand volume ratio is 3%.

Composition of Multi-functional Sucker-rod Pump Lifting Simulation Experiment System

As shown in Fig.1, the multi-functional sucker-rod pump lifting simulation experiment system is composed of electro-hydraulic proportional lift system, process circulatory system, dip simulation system, mechanical connection system and data acquisition and controlling system.

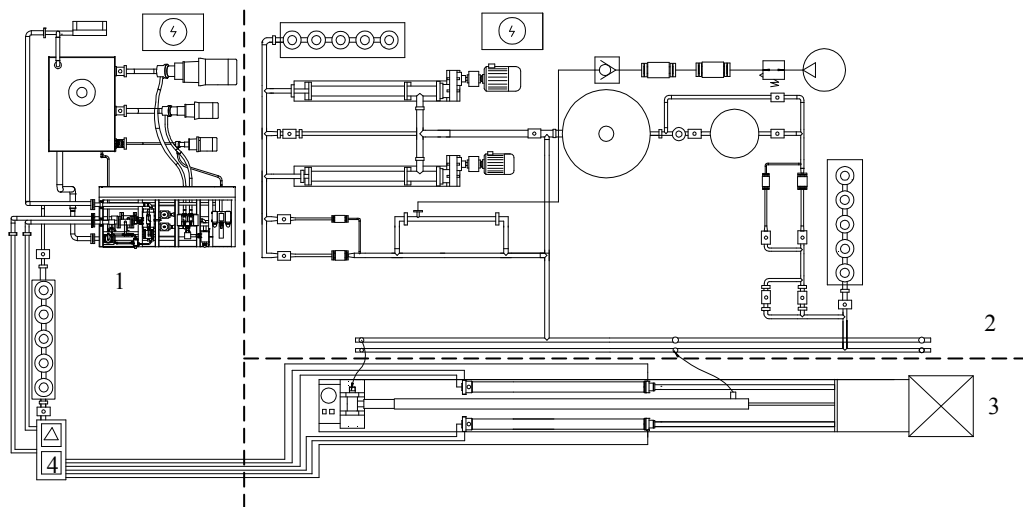


Fig.1 The Schematic Diagram of Multi-functional Sucker-rod Pump Lifting Simulation Experiment System

1-electro-hydraulic proportional lift system, 2- process circulatory system, 3-dip simulation system and mechanical connection system, 4-data acquisition and controlling system

Electro-hydraulic proportional lift system. To achieve better speed control effect, the lift system adopts electro-hydraulic proportional lift system which belongs to liquid power system. This system adopts ladder speed curve planning method to control the moving of hydraulic cylinders according to the set stroke and stroke number, then the hydraulic cylinders drive the sucker rod move repeatedly. The stroke and stroke number are both stepless adjustable. There is automatic operation mode; manual operation mode and safety guarantee mechanism in this system. The main parameter indexes include: the max upstroke polished rod load is 12t, the max down stroke polished rod load is 1.5t, the max stroke is 5m and the max stroke number is 6min^{-1} .

Process circulatory system. Process circulatory system is the core of the whole system. It can realize four experiment processes including routine experiment without simulating submergence depth, routine experiment simulating submergence depth, gas-bearing experiment and adding sand experiment.

1. Routine experiment without simulating submergence depth

As shown in Fig.2, open hand valve SFI, close hand valve SFII without starting liquid supply screw pump. Then the sucker-rod pump sucks test medium from liquid storage tank without simulating submergence depth.

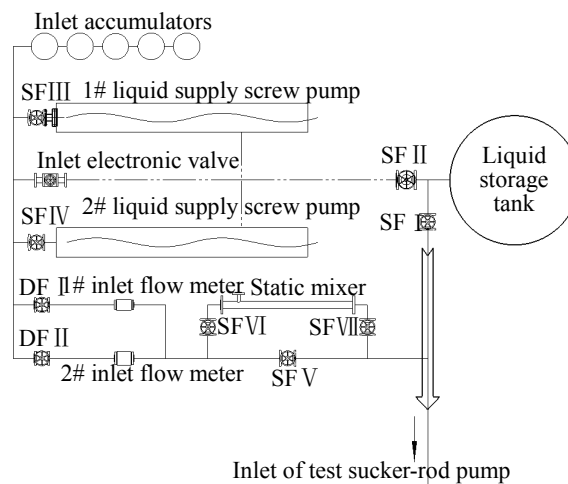


Fig.2 The Schematic Diagram of Routine Experiment without Simulating Submergence Depth

2. Routine experiment simulating submergence depth

As shown in Fig.3, open hand valve SFII and close hand valve SFI. Select 1# liquid supply screw pump ($8\text{m}^3/\text{h}$) or 2# ($16\text{m}^3/\text{h}$) to start according to the pumpage of the test sucker-rod pump and also 1# inlet flow meter ($0\sim 5\text{m}^3/\text{h}$) or 2# ($5\sim 30\text{m}^3/\text{h}$). At the same time, the hand valve SFV should be open and hand valve SFVI and SFVII closed.

Start the selected screw pump to supply test medium for test sucker-rod pump. The inlet pressure of the test sucker-rod pump (namely submergence depth pressure) is regulated through inlet electronic valve opening. The test medium which discharges from the outlet of test sucker-rod pump first flows through the outlet electronic valve that regulates outlet pressure, and then flows through flow meter. Two electronic valves are set in order to realize wide pressure range ($0\sim 15\text{MPa}$) regulation. In addition, outlet accumulators are used in order to keep outlet flow stable and improve precision and stability of outlet pressure.

If electronic valve DFV is open and electronic valve DFVI and DFVII are closed, the outlet flow can be measured through flow meter and the test medium flows back to liquid storage tank directly. If the outlet flow is quite few or the flow meter can't meet the measurement demand, measuring tank is used to measure outlet flow. In addition, the measuring tank can be used to calibrate flow meter. Open electronic valve DFV and close electronic valve DFVI and DFVII, then test medium

flows into measuring tank. While the liquid level reaches a certain height, finishes the measuring process. Then, open electronic valve DFV and close electronic valve DFVI and DFVII to let the just discharging test medium flow to the measuring tank. At the same time, open electronic valve DFVII and start the pipeline pump to let test medium in measuring tank flow back to the liquid storage tank.

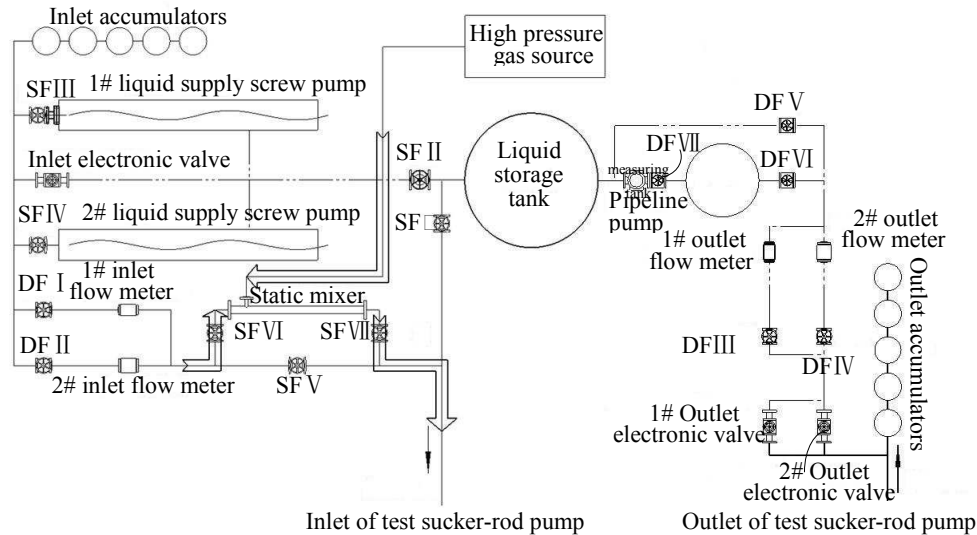


Fig.3 The Schematic Diagram of Routine Experiment Simulating Submergence Depth

3. Gas-bearing experiment

Before the gas-bearing experiment, close hand valve SFV and open electronic valve SFIV and SFVII. Establish the pressure of high pressure gas source and regulate air inflow through throttle valve according to the submergence depth pressure. The liquid and air are mixed by static mixer. The other experiment process is the same as routine experiment.

4 Adding sand experiment

The adding sand experiment process is the same as routine experiment except adding certain amount sand and additive which can increase test medium viscosity and stirring uniformly by agitator before the experiment begins.

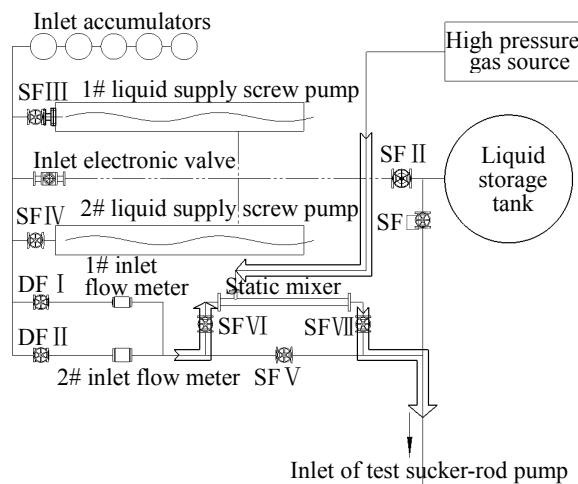


Fig.4 The Schematic Diagram of Gas-bearing Experiment

Data acquisition and controlling system. This system adopts centralized control system, every property parameters and indicator diagram are got through computer acquisition. Experimental results of 57mm oil well pump under Stroke 5m, Stroke number 4min^{-1} , Dip 10° are shown in Table 1 and the indicator diagram is shown in Fig. 5.

Table1 The Experimental Results of 57mm oil well pump
under Stroke 5m, Stroke number 4min^{-1} , Dip 10°

Experiment parameter	Result	Experiment parameter	Result
Average outlet pressure(MPa)	14.124	Average outlet flow(m^3/h)	2.551
Dip($^\circ$)	10.000	Average gas flow into pump(m^3/h)	0.002
Average inlet flow(m^3/h)	2.495	Average inlet pressure(MPa)	2.442
Maximum of polished rod load(t)	2.383	Test medium temperature($^\circ\text{C}$)	29.105
Stroke(m)	4.717	Minimum of polished rod load(t)	-0.947
Discharge coefficient	0.892	Stroke number(min^{-1})	3.959

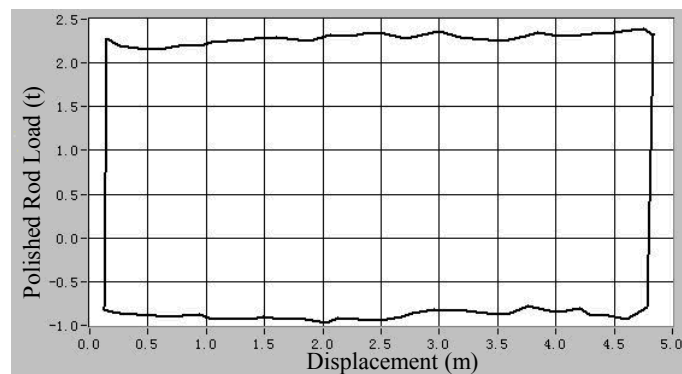


Fig.5 The Indicator Diagrams of 57mm oil well pump
under Stroke 5m, Stroke number 4min^{-1} , Dip 10°

Conclusions

This experiment system can complete the property experiment of sucker-rod pump of which diameter covers 38mm to 140mm. It can simulate the working condition of sucker-rod pump in vertical well, controlled directional well and horizontal well and can detect the major parameters scientifically. Parameters such as stroke, stroke number and discharge coefficient are got through calculating as well as indicator diagramare which provides scientific experiment data for different kinds of sucker-rod pump. Applying this system into oilfield production can raise the scientific management level of sucker-rod pump to a great extent, reduce the production running cost and raise economic benefit significantly.

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Investigation of high pressure water jet with hydraulic reaming drainage radius for coal seam mining

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Key Words: permeability coefficient; hydraulic reaming; hrainage radius

Abstract: Test mine is a large modern mine, the 13-1 coal-seam original permeability coefficient was low, gas pressure and content were higher, coal seam outburst danger of serious, directly extracting coal gas is difficult. Using a new type of high pressure water jet reaming technology, can achieve the expansion of borehole diameter, increase coal seam exposed area and pressure relief range, thereby improving the coal seam permeability, increased coal seam drainage radius. Investigated on the basis of determination of the original coal seam gas pressure and content of the coal extraction radius after the hydraulic reaming. Provide the basis for the seam of the test area borehole design.

1 Mine and general situation of test area

Pan san mine is a design production capacity of 3.0Mt/a large modern mine, the mine production capacity of 5.0Mt/a. Mine East-West length 9.3km, width 5.8km north-south orientation, an area of about 54km². The mine is located in the Huainan synclinerium in Panji anticline in the south, the overall shape is a monoclinic structure. Strata dip general 5 ~10 degrees, a shallow steep deep corrosion tendency. Due to regional north-south extrusion effect, mine is developed secondary fold. The minefield faulted structure more developmnt, local magmatite intrusion, structural complexity of medium. Since building mine outburst accident 14 cases in all, among them cross-hole coal uncovering occurring during the 4 prominent.

Experimental zone 13-1 coal seam stability, thickness of 0.58~ 7.53m, the mean 3.94m, dip angle of coal seam 5~9 degrees. In the east wing area is relatively thick, the average 4.1m, the thinner west average 3.7m, whole area coal seam. Simple structure, there are generally 1~ 2 layer of gangue in coal seam, top or bottom, the lithology as carbonaceous mudstone and shale. Coal seam roof in mudstone and silty sandstone, bottom is sandy mudstone and shale. The corresponding 13-1 coal working face in outburst coal seam outburst danger zone, 13-1 the original coal-seam gas content of about 10m³/t, coal seam gas pressure measure the maximum value is 5.2MPa, the original coal seam permeability 0.0545m²/(MPa²d), the original coal-seam gas pressure, high content, and belongs to the more difficult extraction of coal seam.

2 Drainage radius of investigation principle and scheme

In the construction of the wear layer or bedding coal hole, the drill to drive the high pressure drill and reamer bit rotation, water storage tank high pressure water flows through the hose, high pressure rotary water tail, high pressure pipe and reaming bit nozzle of drilling coal wall blow, cutting or stripping, to enlarge the hole diameter, the exposed area and increase coal seam drill hole radial pressure relief range, thereby increasing the permeability of the coal seam and gas drainage, discharge effect, further reducing the gas pressure in coal seam, at the same time coal bed wetting, coal body coal elasticity, initial velocity of gas is reduced, in order to prevent outburst.

Hydraulic reaming test point is located on the 1792(3) floor lane, in order to improve the test success rate, divided into two groups of 6 holes were arranged, wherein the 4 pressure measuring drill hole. 1[#] and 4[#] hole is hydraulic reaming and gas drainage hole, 1[#] and 2[#] bottom hole spacing 3m, 1[#]

and 3[#] bottom hole spacing 4m, 4[#] and 5[#] bottom hole spacing 5m, 4[#] and 6[#] bottom hole spacing 6m. Two groups between the borehole spacing 7m, namely 6[#] and 2[#] distance 7m. Layout of borehole branch is shown in Fig1.

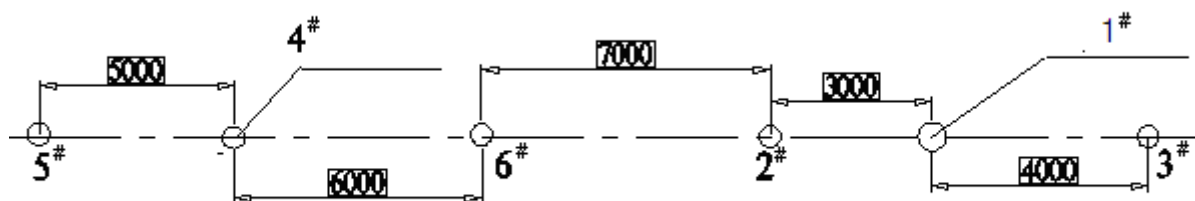


Fig1 Bore sees coal point location plan (unit:mm)

3 Hydraulic reaming drainage radius of investigation

3.1 Investigation of drilling construction and basic parameters

According to the drilling parameters, the first construction of 2[#], 3[#], 5[#] and 6[#] hole, 1[#] and 4[#] pumping hole temporary construction. Construction of hole process, coal sampling for laboratory testing, the basic parameter determination of coal sample the results in Table1:

Table 1 13-1 proximate analysis of coal and gas adsorption constant

ΔP	f	M_{ad}	A_d	V_{daf}	TRD	ARD	F	a	b
5	0.45	1.17	14.74	35.14	1.42	1.61	7	19.2997	0.765

On 2[#], 3[#], 5[#] and 6[#] hole construction is completed immediately after the sealing pressure, drilling construction completed in 7 days, in addition to the 2[#] gauge pressure is 0MPa, the remaining 3 pressure readings are tend to be stable, of which 3[#] pressure gauge observation gas pressure of 2.6 MPa, 5[#] observation gas pressure gauge a pressure of 2.1MPa, 6[#] pressure gauge observation gas pressure of 2.5 MPa. Manometric results are consistent with the actual situation of test area.

3.2 1[#] and 4[#] drainage hole construction and hydraulic reaming

In 4 the pressure gauge readings were stable after the construction of 1[#] and 4[#] pumping hole, after the completion of construction in 1[#] and 4[#] hydraulic reaming. 1[#] drilling shift after the construction is completed, the night shift hydraulic punching test, hydraulic punching effective punching time of 4 hours, the cumulative amount of coal out of 40 bags, about 2.0t. 4[#] drilling shift start hydraulic punching test, effective punching time of 5 hours, the cumulative amount of coal out of 30 bags, about 1.5t.

4 Hydraulic reaming drainage radius determination

Hydraulic punching end, immediate and stubble drainage, drainage negative pressure 13MPa, extraction concentration is 50% ~ 80%; with the extraction time, different distance of gas pressure curve of is shown in Fig2 Fig3 and Fig4:

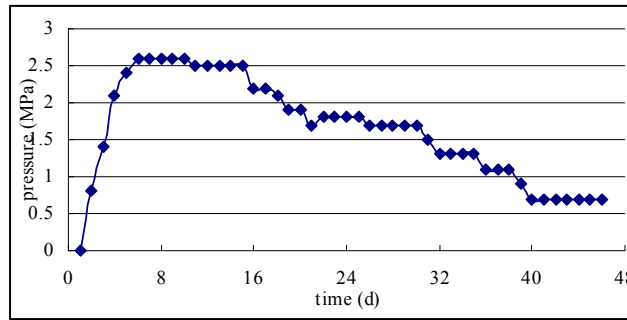


Fig 2 13-1seam drainage radius of 3[#] hole pressure curve

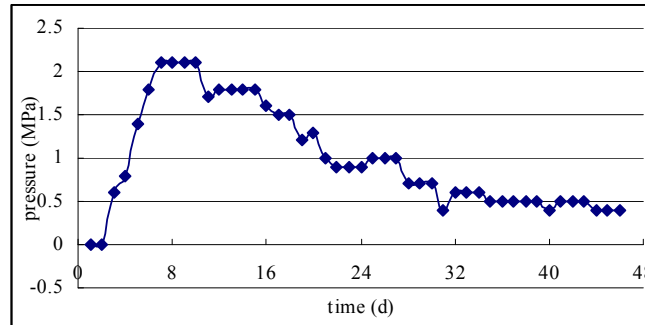


Fig 3 13-1seam drainage radius of 5[#] hole pressure curve

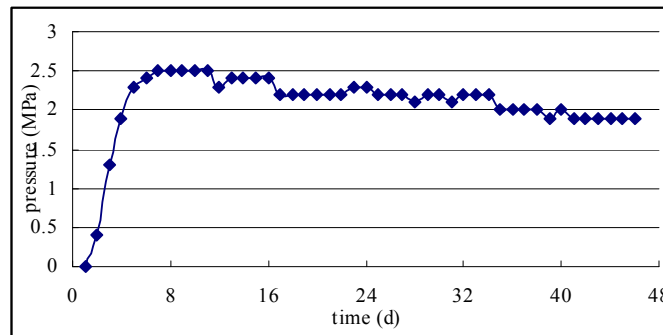


Fig 4 13-1seam drainage radius of 6[#] hole pressure curve

Laboratory Determination of 13-1coal basic parameters extraction before the original gas content was $9.35 \text{ m}^3/\text{t}$, the extraction of 25 days and 40 days of residual gas pressure calculation of regional residual gas content in Table 2 shows:

Table 2 13-1 coal seam gas pressure and hydraulic flushing content change

hole		Reaming drainage before	Reaming drainage (25 days)	Reaming drainage (40days)
3 [#] (4m)	pressure (MPa)	2.6	1.5	0.7
	content (m^3/t)	9.35	7.1	4.5
	decreasing amplitude(%)		24.06	51.87
5 [#] (5m)	pressure (MPa)	2.1	0.7	0.4
	content (m^3/t)	9.35	4.5	3.0
	decreasing amplitude(%)		51.87	67.9
6 [#] (6m)	pressure (MPa)	2.5	2.2	1.9
	content (m^3/t)	9.35	8.55	7.9
	decreasing amplitude(%)		8.56	15.5

By the Fig 2~4 and table 2 calculating results, 1[#] and 4[#] hydraulic punching and close the stubble is mined, 6[#] drilling in punching pumping 40 days later, gas pressure remains in 1.9MPa, residual gas content for 7.9m³/t, the author believes that the 6[#] drilling (and inspection hole bottom distance 6m) do not belong to the reaming drainage radius. 3[#] and 5[#] investigation drilling increased with time gas pressure decreases slowly, drilling drainage in 25 days, 3[#] and 5[#] drill gas pressure drop respectively to 1.5MPa and 0.7MPa, corresponding to residual gas content are respectively 7.1m³/t and 4.5m³/t (less than 8m³/t); drilling drainage 40 days later, the 3[#] and 5[#] drill gas pressure were decreased to 0.7MPa and 0.4MPa (are less than 0.74MPa), corresponding to residual gas content are respectively 4.5 m³/t and 3m³/t, comprehensive analysis showed that 3[#] and 5[#] drilling (3[#], 5[#] drill and inspection hole bottom distance 4m, 5m) in the hydraulic hole effective drainage radius. In summary, study to determine the 13-1 coal seam hydraulic hole after extraction of 40 days the effective drainage radius 5m. The drainage radius is determined, as a test area the Gross measures boreholes in coal seam to provide basis for design and construction of.

5 Conclusions

[1] Using a new type of high pressure water jet reaming technology, can achieve the expansion of borehole diameter, increase coal seam exposed area and pressure relief range, thereby improving the coal seam permeability, increased coal seam drainage radius.

[2] The gas pressure and the content of reducing method, determine the 13-1 coal seam with high pressure water jet hydraulic reaming after extraction of 40 days the drainage radius 5m.

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A Review on Reagents and Processes of Fine-Grained Cassiterite Flotation in Mining Engineering

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Keywords: fine-grained cassiterite, collector, depressant, flotation

Abstract: Tin resources are abundant and complicated in China. Most of tin resources come from cassiterite. Normally the main beneficiation method of coarse cassiterite ore is gravity separation. However, as for the fine-grained cassiterite, flotation and joint processing techniques are generally selected to improve the low recovery from gravity separation. This paper outlines different kinds of cassiterite, collectors and depressants for cassiterite flotation and their using conditions and some reinforced methods in beneficiation of the fine-grained cassiterite for reference in mining industry.

Introduction

Tin ore resources in China are always rich. The reserves and retained reserves rank first in the world. The tin ore mostly centers in Yunnan, Guangxi, Hunan, Inner Mongolia and so on [1]. According to the studies of a number of tin ore bodies, tin can be classified into three major groups [2]: Cassiterite contained in pegmatite veins contain significant quantities of (Nb,Ta)₂O₅ with traces of wolframite and manganese. This type of cassiterite is fragile and tends to slime during grinding; Cassiterite from quartz veins. Cassiterite from this group contains about 1% (Nb,Ta)₂O₅ and about 0.3%-0.4% wolframite; Cassiterite from sulphide veins usually contains vanadium, sulphur and wolframite. The most important tin mineral is cassiterite. According to their floatability, ores and products containing cassiterite can be subdivided into the following three groups [3]: Easy to float ore-typically cassiterite/quartz ores; Moderate to float ore-cassiterite sulphide deposits with small quantities of chlorite, tourmaline and iron oxides; Difficult-to-float ore or sometimes refers to virtually unfloatable ore-these ores contain large quantities of chlorite, topaz, fluorite and limonite. In mining engineering, knowing about the deposit and composition of minerals is a precondition to determine the beneficiation method. The commonly used beneficiation method for coarse-grained cassiterite is gravity separation and for fine-grained is flotation. Sometimes a joint beneficiation of gravity separation and flotation is necessary. The greatest challenges for the beneficiation of fine-grained cassiterite include: the tin losses to slimes, the world tin loss in the slime has reached 5% [3]; the effect of impurities, such as sulphides which will easily be floated with cassiterite.

Flotation Reagents

Collectors

In mining engineering, collectors are a decisive factor for the grade and recovery of final concentrate. The main collectors of cassiterite used on industry are fatty acid, arsenic acid, phosphonic acid alkylhydroxamic acid and alkyl sulfonated succinate. Among these collectors, oleic acid, benzyl arsenic acid and styrene phosphonic acid are frequently used.

Oleic acid is one of the most commonly used fatty acid collectors with a strong collecting ability and a small amount of dosage in cassiterite flotation. But it is short of good selectivity. Oleic acid is sensitive to Fe^{3+} and Ca^{2+} , causing it is easy to be floated with iron minerals, fluorite and calcite. Oleic acid is generally used to concentrate cassiterite-quartz slime in the condition of neutral or alkaline.

The major arsenic acid includes fatty arsenic acid and aromatic arsenic acid, both of which are efficient collectors. Fatty arsenic acid can react with Sn^{2+} , Sn^{4+} , Fe^{3+} and other metal ions and generate insoluble compounds, particularly when at high concentration will react with Ca^{2+} and Mg^{2+} to form salt. When they are used to concentrate ultrafine cassiterite from sulphide minerals which contains gold, it is necessary to remove the slime and sulphur in advance to avoid the concentrate being influenced. Aromatic arsenic is efficient in flotation in weak acid medium. Arsenic acid is toxic and many plants have ceased to use it. Most recently, interest has been renewed in the use of methyl benzyl and a mixture of p- and o-tolyl arsenic acid as cassiterite collector. Zhu Jianguang [6] used benzyl arsenic acid as a collector in the flotation of cassiterite slime of Da Chang Chang po concentration plant. The results have shown that benzyl arsenic acid is a good collector for cassiterite slime. The reagent under the trade name MTAA, which consists of approximately 50:50 of p- and o-tolyl arsenic acid, is now extensively used in cassiterite flotation in China. Mixed toluene arsenic acid is the best collector for cassiterite flotation.

Phosphonic acid can be as effective as arsenic acid, but less toxic and cheaper. It includes aromatic phosphonic acid and aliphatic phosphonic acid. When low price styrene phosphonic acid is used in weak acid or neutral pulp, better flotation index can be obtained, especially for collecting cassiterite, wolframite and rutile. Styrene phosphonic acid (SPA) is the best collector for the flotation of finely disseminated cassiterite and wolframite ores. Data from H. Gruner [7] and U. Bilsing's research work has shown that with SPA it is possible to obtain higher grade tin concentrates containing more than 40% Sn at high recoveries. Concentrate froth with aliphatic phosphonic acid as a collector is non-sticky and easy to be dispersed [4]. Phosphonic acid collectors of aliphatic series apply to concentration of ores containing no Fe^{3+} , Ca^{2+} or Pb^{2+} .

Both some metallic ions found in process water supply and those generated by the minerals present in the pulp may affect the performance of the collectors as well as the surfaces of either cassiterite or gangue minerals by either depressing or activating them. In general, the choice of collectors must consider the water quality.

Depressants

Cassiterite is seldom pure. The main impurities are iron, followed by tantalum, columbium and tungsten. These impurities may enhance or adversely affect the flotation recovery of the mineral. So for fine cassiterite flotation process and even in the whole mining engineering, depressants and collectors are equivalent important. It includes inorganic, such as sodium silicate, sodium fluosilicate, sodium hexametaphosphate, and organic depressants, such as oxalic acid, acetic acid.

The mineral composition of the given gangue from which cassiterite is to be recovered plays a major role in determining the flotation selectivity and ultimately the concentrate's final grade and value. Depressants for certain gangue minerals present in cassiterite are shown in Table1:

Because sodium silicate reacts with Cu^{2+} , Pb^{2+} to form compounds cupric silicate and lead metasilicate in pulp, it can depress quartz activated by copper sulphate and lead acetate [4]. Moreover, sodium silicate can also act as pH regulator for cassiterite flotation. Fluosilicic acid, sodium fluosilicate and sodium fluoride are often used together with vinyl phosphonic acid. Usually a certain amount of sodium fluosilicate is added to reduce the depressing effect on cassiterite caused by Ca^{2+} and Fe^{3+} . In spite of the reaction between sodium hexametaphosphate and polyvalent metallic ions, slime dispersing of sodium hexametaphosphate eliminates negative effects brought by Ca^{2+} and Mg^{2+} .

Table 1 Depressants for certain gangue minerals present in cassiterite

Quartz	Mica	Feldspar	Tourmaline	Topaz	Fe ₂ O ₃	Garnet	Tantalite
Na ₂ SiO ₃	Na ₂ SiO ₃	Na ₂ SiO ₃					
H ₂ SiF ₆	H ₂ SiF ₆			H ₂ SiF ₆			
			Na ₂ SiF ₆			Na ₂ SiF ₆	Na ₂ SiF ₆
NaPO ₃							
H ₂ SO ₄							
NaOH			Oxalic acid		Oxalic acid		
Citric acid					Citric acid		
			Tannic acid				

Some organic depressants need to be used together with certain collectors to produce the best possible result. Carboxymethyl cellulose sodium is usually used together with oleic acid and high price tributyl phosphate. Naphthol sulfonic acid used together with alkyl dicarboxylic acids depresses topaz effectively. A good condition of pH boosts the depressing action. At pH=8.1 the combination of carboxymethyl cellulose sodium and oleic acid depresses calcite most effectively. Hematite contained in the raw ore can be strongly depressed by pyrogalllic acid at pH=3.

Flotation Processes

Agglomerating Flotation

Agglomerating flotation is that, under the effect of neutral oil, some mineral particles agglomerate to coarse oil briquettes or small flocs by hydrophobic agglomerator and then they are separated from the pulp. Wu Bozeng [5], Wang Dianzuo and other men studied the phenomenon of adsorption of sodium oleate on surface of -10 μ m cassiterite and discussed the reliability of adsorption of sodium oleate on surface of ultrafine cassiterite using zeta potential measurement and extended DLVO theory. The results show that aggregation of cassiterite can be improved by sodium oleate in the absence or presence of polyacrylonitrilamide and the recovery of aggregate increases about 5%. When the cassiterite surface is hydrophobic, cassiterite particles aggregate spontaneously.

Selective Flocculation-Flotation

Virtually, selective flocculation is adding heavy polymers into pulp suspension, and the heavy polymers selectively adsorb on some particles and make them flocculate to bigger size to settle down. Other particles are still dispersing. Finally, two kinds of particles are separated by flotation. The key to the method is a selective flocculating agent. Staple polymer flocculants include natural high polymer such as starch and tanning and synthetic polymers such as polyethylene oxide and sodium polyacrylate. Zhong Hong [8] and Zhu Deqing studied the selective flocculation of cassiterite-quartz mixtures. The investigation shows that sulphonated polyacrylamides are the best flocculants for extremely fine cassiterite minerals. Though polyacrylamide can enlarges the small cassiterite flocs, but large mass concentration of polyacrylamide may cause spacial repulsion which is bad for the aggregation of cassiterite particles. In order to improve the selectivity, usually auxiliaries are added for depressing or activating, and they change the surface nature of minerals in advance and make the flocculating agent more selective on different mineral surfaces.

Carrier Flotation

Carrier flotation is that floatable coarse mineral particles are added into the pulp as a carrier, fine-grained particles adhere to the carriers or fine-grained particles themselves flocculate together, then the coarse particles are collected out. For high initial grade cheap minerals the consumption

proportion between carriers and minerals in the sample is relatively low, kindred carriers do fine. But for expensive minerals with low initial grade like tin and tungsten the carrier consumption is relatively high. In actual production, the recovery of carrier itself is hard to reach 100% and kindred carriers cannot promise desirable overall recovering effect. Liang Ruilu [9] and Shi Daxin studied the carrier flotation of ultrafine cassiterite particals through the separation of artificial mixed minerals and resulted in the increase of tin recovery from 51.78% of conventional flotation to 95.77% and 85.08%.

Dissolved air Flotation

Dissolved air flotation for cassiterite especially for cassiterite argillized badly makes economic sense. It uses water supersaturated with air to generate a cloud of microbubbles much smaller than those produced by a conventional dispersed air system. Two defects of the method are coagulation influence aroused by collector adsorption and the cost of air provision. R.J.Gochin [10] and J.A.Solari separated cassiterite from cassiterite-quartz mixture. The results show that dissolved air flotation can be successfully used for fine minerals collecting.

Conclusions

Though various flotation regents can be used for cassiterite separation, a number of difficult problems still cannot be avoided due to bad selectivity, high cost of the reagents, low index and serious environment pollution. Generally, particles between 10 μ m and 37 μ m can be recovered effectively by conventional flotation. But for particles smaller than 10 μ m which is of big surface area and small body, high concentrate grade and recovery wouldn't be obtained because of severe mechanical inclusion of impurities in conventional flotation. Given to the above-mentioned common issues of fine minerals recovery both at home and abroad, researching and developing on new reagents and combined collectors and reinforced methods still make significant sense in mining engineering.

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Study on the Technique to Control Heat-damage in Mine

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Keywords: deep mine, heat-harm control, mine discharge, deep geothermal energy

Abstract: With the increasing of exploitation scope and intensity, the deep mining would be the essential choice, where the heat-harm of high temperature becomes one of the main barriers. Through analyzing the thermal damage feature, the cooling technology were be used that put the mine discharge as cold source to control the heat harm. By disposing three main workstation, the technology can be accomplishes its operations and corresponding functions in different exploitation level. Particularly, the exchanged heat source form the workplace is taken to ground heating by the circulating water which being acted as a carrier. It show that the design concept of this technology include protect the environment and reduce the emission of deleterious air. The results of the project illustrate that the technology to control the heat-harm is efficient. The temperature of the workplace is brought down to 26-29 centigrade, and is 4-6 centigrade lower than the original, and the relative humidity is 5-15 % lower than before. It is greatly improves the working environment of the workplace where the heat-harm of high temperature and high humidity lasts for a quite long time. In addition, it extracts deep geothermal energy successful replacing ground fired boiler for heating, further reducing environmental pollution.

1 Introduction

At present, energy crisis and deterioration of the ecological environment are faced by countries of the world. Under dual pressure of international energy crisis and environmental pollution, people of all countries of the world began to think about relations between human race and the environment from the origin of the ecosystems, actively repairing and compensating for the damaged ecological environment, searching for clean, efficient and new alternative energy (such as solar energy, wind energy, tidal energy) to improve energy structure and decreasing primary energy consumption and pollution emissions. As a green energy, deep geothermal energy includes a great deal of thermal energy, and it could turn to be heat-harm if not being explored and utilized. Most mines in eastern China were explored deeper^[1], while exploration depth increasing, the original rock temperature would rise, and heat-harm on excavation and working face would become more and more serious^[2]. Heat-harm would not only do great harm to physical and mental health of mine workers, but also lead to safety accidents, parts of absorbed gas could be released by environmental temperature increasing and then have a great potential safety problems^[3,4,5]. So it is extremely urgent to control heat-harm.

In this study, we take heating system on ground and mine air condition into account and investigate the possibility of transferring the heat harm to a heat source and delivering this heat source to the ground to replace ground coal-fired boiler^[6,7]. Further investigations were perform to identify the optimum cooling strategy that should be adopted to maintain a satisfactory climate at the working face of the coal mine

2 The previous Heat-harm control system

(1) Central air conditioning system

This cooling system cools water of the unit by spray facilities, sometimes adding auxiliary fans in cooling system, using heat-exchange between wind and water to enhance cooling effect. Cold water of the unit finishes heat-exchanging with intake air flow by passing air cooler, the cooled air flow is

conveyed by fans to working face passing wind tunnel and cool the working face. According to the layout form, central air conditioning system gradually developed into the ground centralized and underground centralized modes. The main problems of this system are large depth, high pressure and high cost; for underground centralized mode, the main problems are heat elimination, weak cooling effect (small circulating water temperature difference, mixed air system) and high operation cost.

(2) Ice cooling system

The ice cooling system use granular ice or mashed ice manufactured by ice maker (pack ice must be processed by chip ice machine), conveys it to underground ice-melting pool, uses water from working face spraying on it to melt the ice, then conveys the cold water to working face and sprays the cold water to reduce temperature. Ice cooling system is mainly comprised with three parts of ice production, ice conveyance and ice melting. Main problems of ice cooling systems are that ice pipelines are easy to be blocked to break operation off; spray cooling would increase humidity; high operation cost.

The above cooling systems all have a most serious problem, they are all energy consumption systems, needing to consume plenty of energy in operation, and could not take use of deep mine heat-harm as a resource, wasting the large number of deep geo-thermal energy. Aiming at taking use of deep mine heat-harm, we designed deep mine geo-thermal energy usage system. This system combines mine water drainage and underground cooling with taking use of heat-harm as a resource, successfully using deep geo-thermal energy to replace ground coal-firing boiler heating, forming a circular green production system with cooling underground and heating on the ground.

3 Experimental Design

(1) Introduction of the coal mine

The coal mine located in Jiangsu province. The mining depth of the coal mine is down to 1000 m and the heat hazard is very serious. The working face temperature is about 37°C and mine water inrush ranges from 600 to 900m/h. Heat for buildings and bath water is supplied by boilers, which wastes plenty of resources and pollutes the environment seriously. The geothermal gradient ranges from 2.25~2.81°C and average is 2.52°C, the temperature of rock at different depth was shown in the Fig.1.

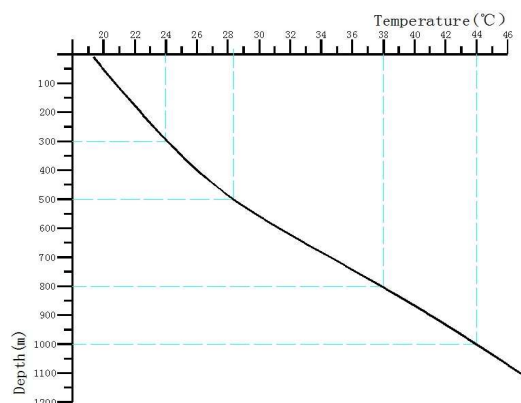


Fig. 1 Distribution curve of ground temperature of the Zhangshuanglou coal mine

(2) Design of cooling system

According to the specific conditions in the coal mine, the optimal cooling system is used to reduce the temperature in this mine. The cooling system uses mine water as the medium, extract deep geo-thermal energy to replace boiler heating on the ground to achieving the purpose of controlling underground heat-harm. Fig.2 is the technology principle diagram. The system is comprised with two parts of underground and on the ground, the underground part includes air cooler station, refrigerator station, pressure conversion station, heat exchange station and pumping station drainage system, ground part includes regulating pond, heating station and water treatment system. Functions of each station and detailed process are described as following:

①Air cooler station conveys cold energy by water-gas heat exchange to working face to be cooled to control heat-harm, at the same time conveying thermal energy to refrigerator station.

②Refrigerator station conveys the produced thermal energy to pressure conversion station at the same time conveying cold energy to air cooler station.

③Pressure conversion station is used for solving liquid high pressure on pipes, at the same time conveying thermal energy produced in refrigerator station to heat exchange station.

④Heat exchange station is used for solving high physical abrasion, high mineralization, strong chemical corrosion, and successfully delivers thermal energy to mine water.

⑤Finally convey deep geo-thermal energy to ground regulated pond by underground pumping station drainage system, and convert low-grade thermal energy to high-grade thermal energy by heating station to heat on the ground, the mine water whose thermal energy is extracted is recycled after passing water treatment system and achieving drainage standards.

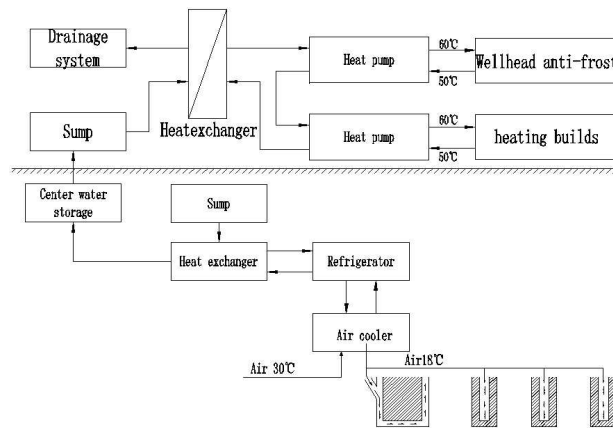


Fig.2 The mine water cooling technology and principle

4 Results and Analysis

The mine water cooling system is successfully applied to the coal mines, the results shows underground cooling effect is significant, heating on the ground is good. The following is the detailed data.

(1) Underground cooling effect

In the operation process, there is a great deal of data featuring system operating status on each day. Data shows that temperature of intake wind on working face is 30.5°C, decreasing to 22.6°C after passing the cooling machine, being 26.4°C when reaching the working face. Controlled temperature at low corner point of working face C is lower by 6°C than that in the same period of 2009, 37°C, meeting the production requirements. Analyzing the data of the whole cooling season, temperature decreasing scope is 4~6°C. The system not only reduces the temperature, but also reduces the humidity by 5~10%.

The overall running effect shows that controlled temperature on working face is between 26~29°C, compared with average temperature on working face before operating the system, controlled temperature after operating system decreases by 4~6°C; relative humidity of intake wind decreased most after passed air cooler, relative humidity of roadway wind continuously rises when conveyed to working face, the relative humidity at controlling point C is 96.4%, and that at air intake vent is 83%. Relative humidity on working face before operating the system is 100%, so after operating the system the relative humidity decreases by 3.6~17%, largely improving working environment for workers.

4.2.2 Ground heating effect

Water temperature supplied for heating designation is 60°C, temperature of returned water is 50°C. The unit ran normally, fully meeting the heating requirements. Diagram 9 shows temperature of water supplied for the unit fluctuates with 60°C, temperature coincidence points of supplied and returned water are automatic off status when temperature of unit reaches the designed 60°C, the unit would restart when heating requirements were not met.

5 Conclusion

In this paper, aiming at deep mine heat-harm and usage of thermal heat through using mine water, get the following conclusions:

(1) by analyzing mines in eastern China, summarize the common problems faced by deep mines and deep mine heat-harm control, and energy waste and environmental pollution due to usage of ground coal-firing boiler.

(2) We successfully develop mine cooling system, which uses mine water as medium, through exchanging thermal energy, achieve use heat-harm as a resource while controlling heat-harm on working face, successfully extracting deep geo-thermal energy to replace ground coal-firing boiler.

(3) Successfully apply to someone coal mines in east China. After applying the system, temperature on underground working face could be controlled between 26~30°C, decreasing about 5~7°C, relative humidity decreasing 5~15%, largely improving working environment on working face with high temperature and humidity for a long time. After ground boiler were replaced by deep geo-thermal energy, coal was saved for 10000t, CO₂ emission was decreased for 17000t, SO₂ emission was decreased for about 100t, with significant energy saving and environmental protection effect.

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The study of numerical simulation about roadway bolting and reinforcement to jointed rock mass

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Keywords: Bolt grouting reinforcement, jointed rock, Numerical simulation, Pressure grouting.

Abstract. Through the mechanical derivation on bolt grouting reinforcement shearing resistance strength of the joint surface, shows that bolt grouting reinforcement focus strengths on the anchor bolt and grouting, and it enhances and elaborates self-supporting ability of rock. Combined with the numerical simulation analysis using the Flac3D software during the jointing soft rock roadway with no supports and protections and bolt grouting reinforcement, we can see that bolt grouting reinforcement has a significant role on improving jointing soft rock roadway force status and limiting roadway rock deformation. Therefore bolt grouting reinforcement is a worthy technology to popularize.

Introduction

Under the affection of higher engineering stress, surrounding rock shows the soft rock properties, and marked diastrophism and expansion happened to structural plane leading to significant deformation of surrounding rock. A large number of engineering practice showed that almost all of the underground engineering failure is result of engineering activities in rock mass which generated stress redistribution. Or, due to deteriorate of geological conditions, it leads to constantly creep evolution on intermittent structure surfaces, resulting the further expansion of crack, even through each other, making different extent deformation and damage on the surrounding rock. Thus affecting the stability of surrounding rock^[2] such as underground mine roof fall, coal seam, floor heave deformation and instability phenomenon, it will harm of mine safety production. Aiming at this problem, the traditional underground mining roadway is generally adopt a means of prestressed anchor reinforcement, and widely applied in underground engineering. But there still exist many shortcomings such as: stress relaxation of anchor itself, low transverse shear strength, the stress excessively concentration. How to make up the deficiency is an urgent need to solve the key. Pressure grouting^[3] as one of the prestressed anchor reinforcement measures, uses a directional grouting technology to press grout into joints, fissures and fault age in order to come up cementation. From the mechanism of grouting reinforcement of surrounding rock^[4-5], we can know that injecting slurry will improve the rock strength and act on bolt joint, remedied the damage of joint fissure, and compared with the original structure of jointed rock mass, the shear strength and shear rigidity is improved greatly.

Given the characteristics of Flac3D to simulate elastic model, nonlinear plastic elastic and other material model, effectively simulate the joint fracture and problem of bolt supporting form, this paper take a underground metal mine roadway as model, revealing the bolt-grouting to improve the joint soft rock roadway surrounding rock stress condition, and it has the obvious effect to limit the distortion of surrounding rock.

1. The tunnel model of numerical calculation

(1) Model establishment. Using large-scale numerical simulation software FLAC3D, this paper established the three-dimensional numerical model, simulated mine roadway tunneling and supporting construction. The model x direction is 30m long; y direction is 3 m long; z direction is high 30m. The model is divided into 1056 units, 1647 nodes; wherein the Y forward direction is roadway excavation advance direction.

(2) Numerical simulation mechanical parameters (Table 1). In various models, the Monorail Transport roadway width is $L = 3700\text{mm}$, $H = 3500\text{mm}$ in high;

Table 1 Mechanical parameters of jointed rock mass

Parameter name	bulk modulus	shear stress	internal friction angle	cohesion	tensile strength
parameter values	27Mpa	7Gpa	350	15.3Kpa	0.076 Mpa

(3) Boundary conditions. According to the actual mining experience and mining theory, model boundary applies uniform vertical compressive stress on both sides; model applies horizontal compressive stress; model surface is displacement constraints; left and right are lateral displacement boundary constraint.

2. Tunnel surrounding rock stress cloud chart analysis

Figure1 and Figure2 respectively for tunnel excavation is supporting and implementation of bolt-grouting rock X direction stress nephogram. As can be seen from the graph, roadway surrounding rock after excavation, attachment exists certain tensile stress, but the value is very small, not enough to reach the surrounding rock failure state of surrounding rock, from more distant in compressive stress state, resulting in less damage, in the overall stability of roadway. Roadway excavation without supporting conditions, over the roadway roof, bottom and two sides appears pulling stress concentration phenomenon. The peak stress is $4.10 \times 10^4 \text{Pa}$, where the roadway two help tensile stress concentration range that is greater than the roadway roof, bottom taking second place. Adopting bolt-grouting reinforcement, the influence range under tensile stress two sides of the roadway is obviously reduced, the peak value is $3.81 \times 10^4 \text{Pa}$, top floor stress concentration range is obviously reduced, and the bottom plate tensile stress exists still. Overall, in the two roadway conditions, X direction stress range is small; supporting role is not very obvious; surrounding rock under tension is insufficient to destroy the rock itself tensile stress; rock won't appear bigger damage of surrounding rock stability; the overall effect is good

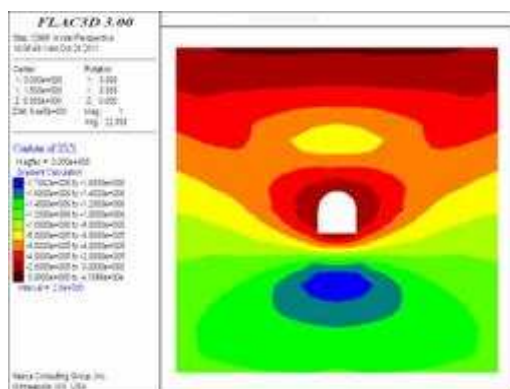


Fig 1 X direction stress nephogram before support roadway

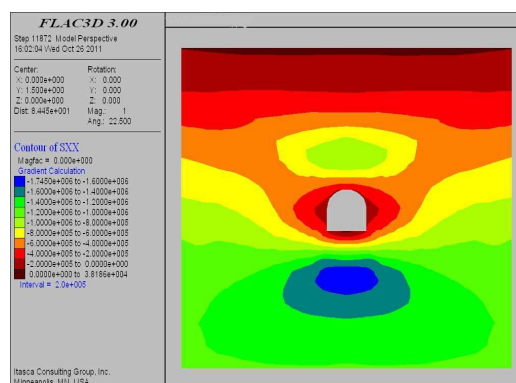


Fig 2 X direction stress nephogram after bolt-grouting

Figure3 and figure4 respectively for tunnel excavation is not support and implementation of bolt-grouting reinforcement after rock Z direction stress nephogram. As can be seen from the graph, Z direction stress range are basically in the compressive stress after excavation; tensile stress area is very small, not enough to destroy the rock mass. Roadway in excavation without supporting condition, the roadway roof, floor and two sides appear small tensile stress concentration; the peak value is $4.8 \times$

10^4 pa, the floor and the roof surrounding rock affected by stress concentration effect, two sides of the roadway surrounding rock take second place. Adopting bolt-grouting reinforcement, support changed the stress state of the surrounding rock, making jointed soft rock roadway in rock fracture closure; overall situation improved. Through the stress analysis, roadway roof rock stress of roadway floor disappeared, and two shoulder surrounding rock stress range is greatly reduced; its maximum is 4.3×10^4 pa; the stress can be neglected. From the Z direction of rock tensile stress nephogram distribution situation, roadway with bolting support, greatly improve the surrounding rock stress state, played a very good supporting effect, the joint soft rock supporting positive role.

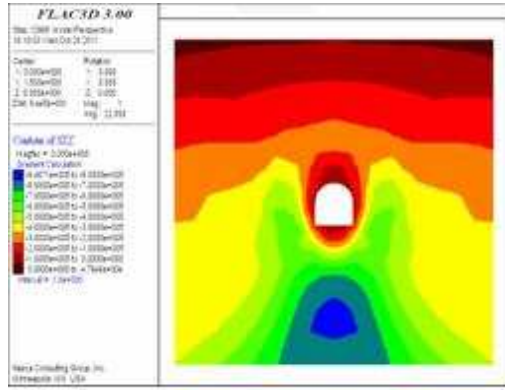


Fig 3 Z direction stress nephogram before support roadway

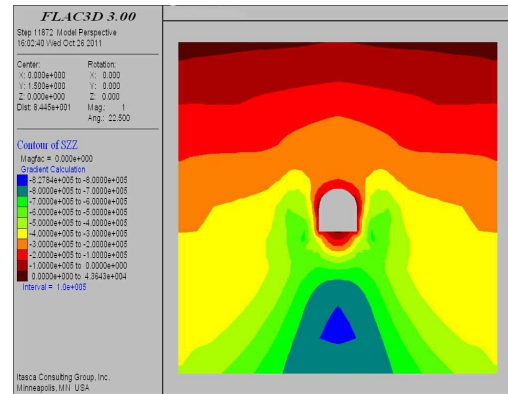


Fig 4 Z direction stress nephogram after bolt-grouting

Through two kinds of roadway surrounding rock stress nephogram, we can know that bolt-grouting roadway surface stress concentration degree is reduced significantly; high stress transfer to deep rock mass, therefore it is beneficial to the self bearing capacity, thus it is conducive to the maintenance of the roadway. From the surrounding rock damage region morphology can be seen, bolt-grouting reinforcement of rock strength was significantly improved; tensile stress failure depth was significantly smaller; it prevent loose surrounding rock from breaking to the deep development in the long term, more conducive to tunnel stability.

3. Roadway surrounding rock displacement analysis

Fig 5 and Fig 6 respectively are X direction displacement nephogram which are not supporting and bolt-grouting in roadway surrounding rock after tunnel excavation. Roadway excavated without supporting; roadway surrounding rock in left moved 8.0×10^{-2} m; roadway surrounding rock in right moved -8.0×10^{-2} m. Adopting bolt-grouting reinforcement of roadway surrounding rock, tunnel surrounding rock displacement around two sides has significantly changed. Roadway surrounding rock in left moved 4.0×10^{-2} m; roadway surrounding rock in right moved -4.0×10^{-2} m. By the data, displacement in two sides has reduced 50% after adopted bolt-grouting reinforcement. This shows that the bolt-grouting support to prevent wall caving plays a certain effect, bolting and grouting has a obvious effect.

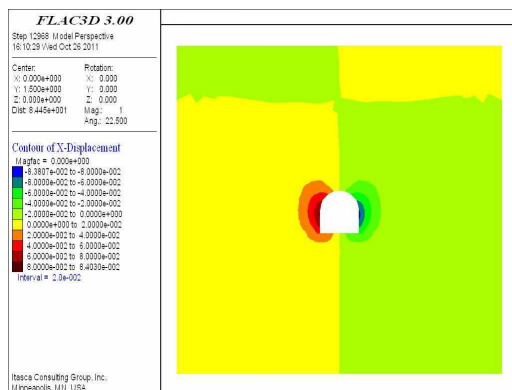


Fig5 X direction displacement nephogram before support roadway



Fig6 X direction displacement nephogram after bolt-grouting

Fig 7 and Fig 8 respectively are Z direction displacement nephogram which are not supporting and bolt-grouting in roadway surrounding rock after tunnel excavation. Roof descended 5.88×10^{-2} m after tunnel excavation; soleplate maximum base expansion is 8×10^{-2} m. Adopting bolt-grouting reinforcement of roadway surrounding rock, roof squat is 5.88×10^{-2} m after tunnel excavation; moreover soleplate maximum base expansion is 7.0×10^{-2} m. This shows that the bolt-grouting support to protect roof plays a certain effect; but bottom expanding volume is still relatively large result from no installation corner bolt.

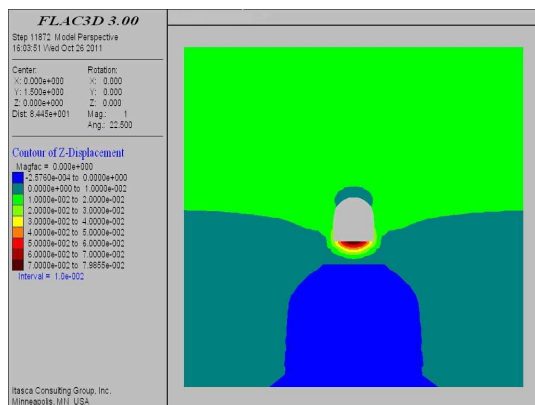


Fig 7 Z direction displacement nephogram before support roadway

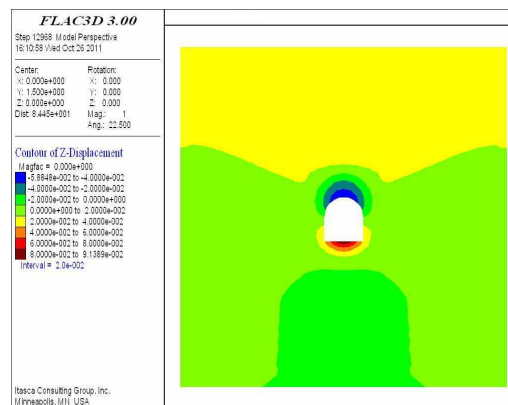


Fig 8 Z direction displacement nephogram after bolt-grouting

4. Conclusion

- 1) Through the shear strength of mechanical derivation about the joint surface with bolt-grouting reinforcement, we can obtain mechanism of action about bolt-grouting support in jointed rock mass, revealing the strengthening about bolt-grouting reinforcement of jointed rock mass.
- 2) Based on the calculation on jointed rock mass with bolt-grouting reinforcement which is simulated by Flac3D numerical simulation software, the paper demonstrated: bolt-grouting reinforcement to improve the stress condition about joint soft rock roadway surrounding rock, limit the amount of deformation of roadway has a major role in jointed rock masses for jointed rock masses, bolt-grouting is an effective supporting method. This is technically feasible, and this method can give full play to the role of bolt and grouting of double effect, thereby avoiding the disadvantages of single function of bolt.

Acknowledgements

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Effect of Pore Pressure Variation on Borehole Stability of Drilling in Sandstone Reservoir

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Keywords: porosity; effective stress factor; caving pressure; fracturing pressure

Abstract. Considering pore pressure variation of sidewall rock, which is caused by drilling fluid filtering, the porosity variation model of sidewall rock in sandstone reservoir and effective stress factor variation model are established, and according to relationship between pore pressure and total volume strain of sandstone, the calculation model of safe window of drilling fluid density on sandstone reservoir, with which considered variation of porosity and effective stress factor are finally established. Applying the calculation of this model shows that: with increased function of drilling fluid filtering, which is as increased as pore pressure of sidewall rock, caving pressure that ensures well hole stability is increased, fracturing pressure is decreased, safe window of drilling fluid is narrowing, and that is against of safety drilling.

Introduction

The study of borehole stability is always hot issue in oil drilling field. Many scholars have made important achievement in many aspects, such as the sidewall stress distribution, and the effect of mechanic-chemical coupling, temperature and pressure on sidewall stability [1-3]. However, the effect of pore pressure variation on porosity, effective stress factor and borehole stability, has not been proved in theory. The author established the model for calculating safe density window of drilling fluid considering the effect above, and explained the effect of pore pressure variation on borehole stability.

1 Pore pressure variation of sidewall rock caused by drilling fluid filtering

In the process of drilling, the function of drilling fluid filtering can cause pore pressure variation of sidewall rock, which can cause the deformation of rock media, and cause porosity variation, the porosity change from the initial value φ_0 to φ :

$$\varphi = \frac{(V_{b0} - \Delta V_b) - (V_{s0} - \Delta V_s)}{V_{b0} - \Delta V_b} \quad (1)$$

where: V_{s0} is the initial volume of the rock solid skeleton, m^3 ; V_{b0} is the initial value of the rock total volume, m^3 ; ΔV_s is the fluctuating value of the rock solid skeleton volume, m^3 ; ΔV_b is the fluctuating value of the rock total volume, m^3 .

We can get the porosity that has changed by Eq. 1 and combining the definition of the rock total volume strain ε_v and rock skeleton volume strain ε_s .

$$\varphi = \varphi_0 - (1 - \varphi_0) \frac{\varepsilon_v - \varepsilon_s}{1 - \varepsilon_v} \quad (2)$$

We can get Eq. 3 according to the definition of rock pore compressibility factor and considering the variation of the skeleton volume.

$$C_{\varphi} = \frac{1}{\Delta p} \cdot \ln \left[\frac{\varphi_0 + \varepsilon_v}{\varphi_0 (1 + \varepsilon_v)} \right]. \quad (3)$$

The relationship between rock pore compressibility factor C_{φ} and pore volume compressibility factor C_p and skeleton volume compressibility factor C_s is [4]:

$$C_{\varphi} = (1 - \varphi_0)(C_p - C_s). \quad (4)$$

We can get Eq. 5 by substituting Eq. 3 into Eq. 4, and combining the relationship between rock pore volume compressibility factor and skeleton volume compressibility factor that has been derived by Chuanliang Li [5].

$$\varepsilon_s = \frac{1}{2\varphi_0 - 1} \cdot \ln \left[\frac{\varphi_0 + \varepsilon_v}{\varphi_0 (1 + \varepsilon_v)} \right]. \quad (5)$$

We can get the porosity that has changed by equation Eq. 5 and Eq. 2.

$$\varphi = \varphi_0 - \frac{(1 - \varphi_0)}{(1 - \varepsilon_v)(2\varphi_0 - 1)} \left\{ \varepsilon_v (2\varphi_0 - 1) - \ln \left[\frac{\varphi_0 + \varepsilon_v}{\varphi_0 (1 + \varepsilon_v)} \right] \right\}. \quad (6)$$

If the skeleton volume strain is ignored, the changed porosity can be simplified by Eq. 2.

2 Sandstone effective stress factor variation caused by the variation of the porosity

Zhonggao Ma draw a conclusion that Biot coefficient has a good power index relationship with porosity by summary predecessors' experience and experimental research [6].

$$\alpha = \begin{cases} \left(\frac{\varphi}{\varphi_c} \right)^n, & n = \frac{2}{3} & \varphi \leq \varphi_c \\ \alpha = 1 & & \varphi > \varphi_c \end{cases} \quad (7)$$

Where: φ_c is critical porosity, for sandstone $\varphi_c \approx 0.4$.

For the general sandstone reservoir, we can get dynamic change model for calculating Biot coefficient by substituting Eq. 6 into Eq. 7.

$$\alpha = 1.842 \cdot \left(\varphi_0 - \frac{(1 - \varphi_0)}{(1 - \varepsilon_v)(2\varphi_0 - 1)} \left\{ \varepsilon_v (2\varphi_0 - 1) - \ln \left[\frac{\varphi_0 + \varepsilon_v}{\varphi_0 (1 + \varepsilon_v)} \right] \right\} \right)^{\frac{2}{3}}. \quad (8)$$

If the skeleton volume strain is ignored, the model can be simplified by substituting Eq. 2 into Eq. 7.

3 The relationship between the total volume strain of sandstone and sidewall pore pressure

In the process of drilling, the drilling fluid seepages into the ground under pressure difference, the pore pressure of sidewall rock will increase, Yingtao Yang [7] got the the basic differential equation for describing the relationship between total volume strain of sandstone and pore pressure according to seepage theory.

$$\frac{\partial \varepsilon_v}{\partial t} - (1 - \varphi_0) \frac{\partial \varepsilon_s}{\partial t} - \frac{\varphi_0}{E} \frac{\partial p_p}{\partial t} = 0. \quad (9)$$

We can get the relationship between the value of pore pressure variation and the total volume strain of the rock by integrating Eq. 9 and combining with Eq. 5. Moreover, in order to calculate easily, we can ignore the skeleton volume strain and integrate Eq. 9.

4 The determination of safe window of drilling fluid density considering pore pressure variation

We derive the equation for calculating ρ_m , ρ_f under the condition that the overburden stress is intermediate principal stress considering that the function of drilling fluid filtering can cause the stress redistribution of sidewall rock.

$$\rho_m = \frac{\left((1 - \nu)(1 - \sin \psi)(\sigma_h - 3\sigma_H) + 2C_0(1 - \nu) \cos \psi + p_p [\alpha(1 - 2\nu - 3 \sin \psi + 4\nu \sin \psi) + 2\varphi(1 - \nu) \sin \psi] \right)}{H[\alpha(1 - 2\nu)(1 - \sin \psi) + 2(1 - \nu)(\varphi \sin \psi - 1)]} \times 100. \quad (10)$$

$$\rho_f = \frac{(3\sigma_h - \sigma_H)(1 - \nu) - [\alpha(2 - 3\nu) + \varphi(1 - \nu)]p_p + S_t(1 - \nu)}{H[(1 + \varphi)(1 - \nu) - \alpha(1 - 2\nu)]} \times 100. \quad (11)$$

Where: ρ_m , ρ_f is caving pressure and fracturing pressure that is convert to the density of drilling fluid respectively, g/cm³; C_0 is the cohesive force of rock, MPa; H is the well depth, m; ψ is the internal friction angle of rock; S_t is the tensile strength of rock, MPa; σ_H is the level maximum principal stress, MPa; σ_h is the level minimum principal stress, MPa; p_p is the pore pressure after drilling fluid seepages, MPa; φ is the porosity after the pore pressure changes; ν is the poisson ratio of rock; α is the effective stress coefficient after the pore pressure changes.

5 Calculation example

The calculating data is shown in table 1, the caving pressure and fracturing pressure is calculated by using the model, the calculated result is drawn curve and the curve is in figure 1.

Table 1 Data of X well

well depth (m)	overburden stress (MPa)	minimum stress (MPa)	maximum stress (MPa)	tensile strength (MPa)	cohesive force (MPa)	angle of internal friction (°)	young's modulus (MPa)	poisson ratio	porosity	pore pressure (MPa)
1288	28.153	22.027	35.052	1.2	11.4	38.3	7660	0.2	0.2	12.42
1731	38.597	29.631	49.906	3.31	22.1	34.14	10060	0.19	0.19	17.89
1798	40.212	29.714	49.392	3.2	20.67	34.44	10900	0.17	0.19	18.03
1847	41.4	32.508	55.403	2.28	27.76	24.2	12850	0.14	0.19	18.27

The caving and fracturing pressure curve 1, 2, 3 is obtained at the condition of 1.0, 1.1 and 1.2 times initial pore pressure. We can conclude from the result that with the pore pressure of sidewall rock increasing, caving pressure is increasing, fracturing pressure is decreasing, safe window of drilling fluid is narrowing. In the process of making a trip, it can produce pressure surge in the well, if the safe window is narrow, especially for the reservoir that is easily collapsing and leaking, the borehole will be instability, so the wall building property of the drilling fluid must be improved, reducing the effect on the borehole stability which is caused by drilling fluid filtering.

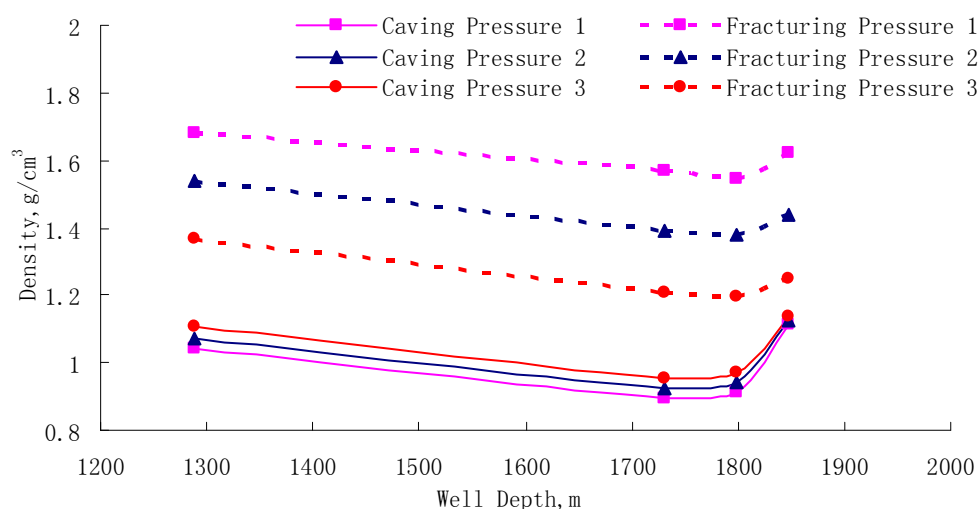


Fig.1 The safe window of drilling fluid density change curves of different pore pressure

Conclusions

In the process of drilling, the function of drilling fluid filtering can cause pore pressure variation of sidewall rock, which in turn can cause the mechanic parameters variation of the rock, such as porosity and effective stress factor. Moreover, with the pore pressure of sidewall rock increasing, caving pressure is increasing, fracturing pressure is decreasing, safe window of drilling fluid density is narrowing, and it will be against borehole stability.

Acknowledgements

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The Effect of Technological Parameter on the Co-liquefaction of Coal with Lignin

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Abstract. The co-liquefaction of coal with lignin was studied by minisize high pressure reactor, tetralin and Fe₂O₃ were used as solvent and catalyst, and the study was focused on the reaction temperature, initial pressure of hydrogen and mixture ratio of lignin with coal. The results showed that the reaction temperature, the initial pressure and mixture ratio has the important influence on the conversion rate of coal, the oil production rate in the process of co-liquefaction with coal and the lignin. Effect of co-liquefaction is best in reaction temperature 440°C, initial pressure 9Mpa, mixture ratio of lignin and coal for 2:8, the conversion rate of coal and the oil production rate respectively achieves 87.66% and 50.39%.

Introduction

The studies for co-liquefaction of coal and biomass were made some progress, but the study of co-liquefaction about coal and agricultural waste such as straw, coal and industrial waste such as lignin was a few in world, especially in China. Influencing factor on the mechanism and the process of co-liquefaction are not entirely clear. Therefore, a large number of experimental data were collected so as to make theoretical research, the establishment of liquid dynamic

The experimental results and discussion

1. The effect of reaction temperature on co-liquefaction of coal and lignin

The effect of reaction temperature was studied on co-liquefaction of shenhua coal and lignin under the conditions that tetralin as solvent, mixture ratio of lignin and shenhua coal for 2:8, cold hydrogen pressure for 9MPa, the reaction time for 60min. The results showed that in Figure1.1 and Figure 1.2.

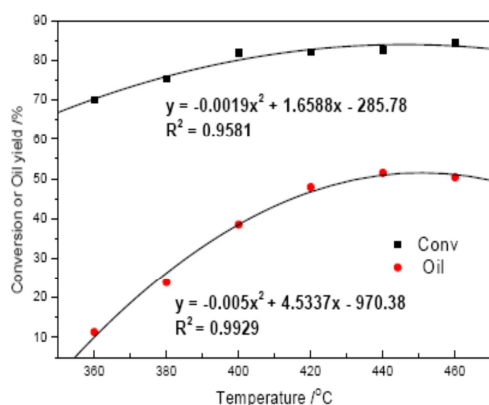


Fig.1.1 Effect of reaction temperature on co liquefaction

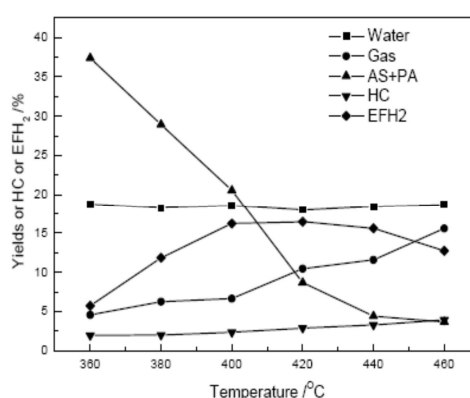


Fig.1.2 Effect of reaction temperature on co liquefaction

From Figure 1.1, with the temperature increasing, the conversion of coal and oil yield is greatly improved, especially the increase of oil production rate is large, the conversion rate of coal increased from 70.12% to 84.42% when the reaction temperature increased from 360 °C to 460 °C, and the increase achieved 14.3%. Oil production rate increased obviously from 11.34% to 51.49%, an increase achieved 40.15%. But oil yield decreased at 460 °C. In figure 1.1, the variation of the conversion and oil yield with temperature was fitted by the use of polynomial.

The variation of conversion with temperature is for $y = -0.0019x^2 + 1.6588x - 285.78$, $R^2 = 0.9581$; the variation of oil production rate with temperature is $y = 0.005x^2 + 4.5337x - 970.38$, $R^2 = 0.9929$, Thus it can be seen that the effect of fitting was very good; the conversion of coal and oil production rate can be predicted by these two equations.

From figure 1.2, the yields of asphaltene and pre-asphaltene increases in the process of co-liquefaction of coal and lignin at a lower temperature. These indicated that reaction at low temperature was cracking reaction from reactants to Macromolecular asphaltene and pre-asphaltene. Asphaltene cracked into smaller fragments of free radicals with temperature increasing, and oil material generate under the action of hydrogen. Three factors affecting the oil production rate: the conversion, asphaltene and pre-asphaltene yield, gas yield.

Figure 1.1 and Figure 1.2 shows that, with the temperature increases, the conversion of coal increased the production rate of asphaltene and pre-asphaltene reduced. It is benefits to improve the oil yield, but production rate of gas increased with temperature increasing. And the increasing of gas production rate caused the reduction of oil production. So choose the right temperature, the product rate of oil can reach the maximum value. The consumption of Hydrogen increases with the temperature increasing, this mainly due to cracking of coal molecules faster, the free radical in cracking reaction consumed more active Hydrogen. The analysis shows that the suitable co-liquefaction temperature is around 440 °C.

The effect of temperature on gas production distribution in co-liquefaction reaction were studied under the condition that tetralin was used as Hydrogen-donor Solvent, the mixture ratio of lignin and shenhua coal is 2: 8, the pressure of hydrogen is 9MPa, the reaction time is 60min. the result showed that Table 1.1 and Fig 1.3.

Table 1.1 Effect of reaction temperature on gas of co-liquefaction

Temp/°C	CH ₄ %	C ₂ H ₆ %	C ₃ H ₈ %	C ₄ H ₁₀ %	C ₅ H ₁₂ %	CO %	CO ₂ %
360	0.75	0.00	0.31	0.65	0.00	0.00	2.86
380	1.37	0.00	0.41	1.10	0.02	0.00	3.36
400	1.58	0.04	0.73	1.15	0.12	0.00	3.04
420	2.56	0.05	1.49	2.30	0.25	0.17	3.66
440	3.69	0.07	1.99	2.33	0.28	0.28	2.96
460	5.56	0.08	3.24	2.83	0.79	0.30	2.80

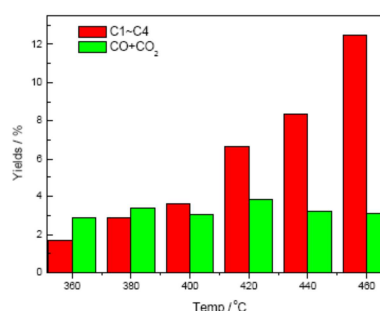


Fig.1.3 Effect of reaction temperature on gas of co-liquefaction

Table 1.1 and Fig 1.3, the production of resultant gas increased with the temperature increasing except CO₂, and the increment of CH₄, C₂H₆, C₃H₈ is significant, but C₂H₄, C₄H₁₀, CO is not. In Fig 1.3, the change of the yield of CO with CO₂ is little, but the yield of lower hydrocarbon increase obviously. The yield of CO with CO₂ is higher than lower hydrocarbon's below 380°C, but yield of lower hydrocarbon increase obvious with the temperature increasing, which is higher than CO with CO₂ when the temperature is beyond 400 °C. The gas increase obviously in 460 °C especially CH₄ and C₂H₆. The result show that cracking and polycondensation strengthen in 460°C and the forming oil production begin to crack and polycondensation, so lower hydrocarbon increase obviously. The effect of temperature is little on CO and CO₂, the removal of CO₂ completed basically in 380°C, and CO₂ combined with hydrogen to form CO, when the temperature further increase.

2. The effect of initial pressure on co-liquefaction of coal and lignin

The effect of initial pressure of hydrogen was studied in 425°C, the tetralin is Solvent, the mixture ratio of lignin and shenhua coal is 2: 8, the reaction time is 60min. the result showed that Table 2.1 and Fig 2.2.

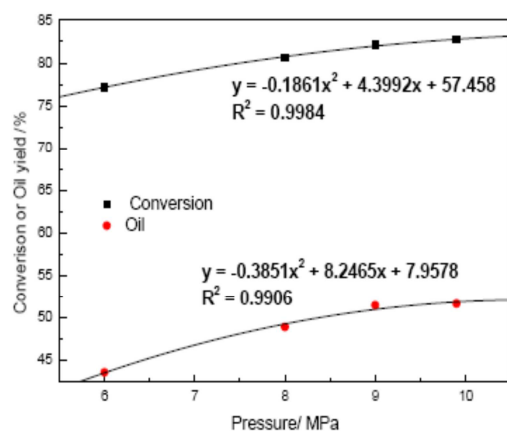


Fig.2.1 Effect of reaction pressure on co-liquefaction

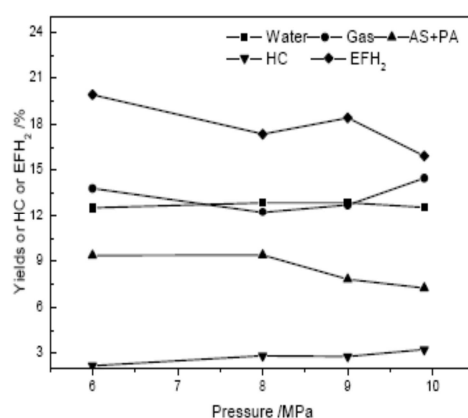


Fig.2.2 Effect of reaction pressure on co-liquefaction

In figure 2.1, the trend of the conversion and oil yield is ascending with initial pressure of hydrogen increasing, but the trend became alleviation with the pressure increasing. The conversion of coal and yield of oil increase obviously when the initial pressure of hydrogen change from 6MPa to 8MPa, the change is 3.48% and 5.3%. The trend is little when changing from 9MPa to 10MPa. The result shows that the effect of initial pressure is little on co-liquefaction when pressure is beyond 9MPa.

In figure 2.2, the variation of the conversion and oil yield with pressure was fitted by the use of polynomial. The variation of conversion with pressure is for $y = -0.1861x^2 + 4.3992x + 57.458$, $R^2 = 0.9984$; the variation of oil production rate with pressure is $y = -0.3851x^2 + 8.2465x + 7.9578$, $R^2 = 0.9906$. It can be seen that the effect of fitting was very good; the conversion of coal and oil production rate can be predicted by these two equations. The change of water yield is about 20%, it is little. the yields of asphaltene and pre-asphaltene decreased about 2.13% with the pressure of hydrogen increasing. Considering economic cost and equipment operation condition, the choice of 9MPa is suitable for co-liquefaction.

3. The effect of mixture ratio on co-liquefaction of coal and lignin

Effect of the amount of lignin was studied on co-liquefaction, the temperature of reaction is 425 °C, the weight ratio is 3: 2 about tetralin with material, the pressure of hydrogen is 8MPa, the catalyst is Fe₂O₃ and S, the time of reaction is 60min. the experimental results show from 3.1.

The figure 3.1 show that the conversion of coal change from increasing to decreasing with the amount of Lignin increasing. When the amount of Lignin change from 0: 10 to 2: 8, the conversion of coal change from 83.35% to 85.9%, the conversion begin to decrease with amount of lignin further increasing. The change of oil yield present the trend of decrease with the amount of lignin increasing, the change is from 60.63% to 11.14%. The trend of gas yield is increasing, Asphaltene and the consumption of hydrogen decreasing, but the change is little. The experimental data of co-liquefaction is compared with the arithmetic mean to prove the promotion of lignin on co-liquefaction, the experimental results show in figure 3.2.

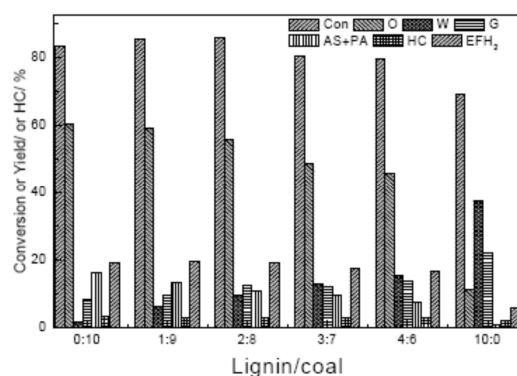


Fig.3.1 The effect of lignin/coal ratios on co-liquefaction

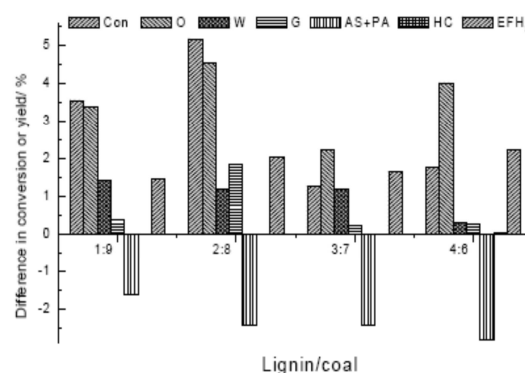


Fig.3.2 The difference Experimental and Arithmetical average values

In figure 3.2, the difference is positive from experimental data and the arithmetic mean, this showed that the conversion and oil yield in co-liquefaction is higher than single-coal liquefaction; co-liquefaction is lower than single-coal liquefaction about the yield of the asphaltene and pre-asphaltene. When the mixture ratio of lignin and shenhua coal is 2: 8, the conversion and the oil yield improve obviously, which is respectively 5.18% and 4.56%. The experimental data show that the addition of lignin promoted decomposition of the asphaltene and pre-asphaltene, the liquefaction effect of coal improved, the yield of oil increased. The yield of water increased in co-liquefaction with lignin increasing, because lignin contains a large of oxygen to make the amount of oxygen increase in the system of co-liquefaction.

Conclusion

Lignin can promote obviously liquefaction of coal, the improvement of conversion of coal and oil yield is significant. The results show that the optimum proportion of lignin and shenhua coal is 2: 8, the optimum temperature of co-liquefaction is 440°C, the optimum initial pressure of hydrogen is 9MPa.

A Study for Piping Phenomenon of the Different Graded Sands on Slope in Mining Engineering of Civil Construction

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Keywords: graded sand, piping phenomenon, critical hydraulic gradient, mining engineering, civil construction

Abstract: In this study, the slope piping experiment selected 6 different sands in mining engineering of civil construction. In addition to discussing the physical parameters of the graded sands in mining engineering, the piping destruction parameters of different slopes were obtained from the experiment. When piping occurs, we can use numerical model to get the hydraulic gradient value at the failure point. The difference between the theoretical estimation and the numerical model was compared and we found that different particle size distribution caused the main difference. The particle size parameter ratio, D^* , is used for correcting the critical hydraulic gradient value in this study. We learned the correction coefficient of D^* is between 0.5~0.857 in different tests and its value approximates the reciprocal of the coefficient of uniformity. Therefore, the critical hydraulic gradient estimation formula for the slope piping of the uniform sand can be future corrected, and it can be used for estimating the graded sand in this study. In civil engineering the sand filling project can use the estimation formula of this study to calculate the critical hydraulic gradient as the reference for design and disaster prevention.

Introduction

The rapid rise of the internal groundwater level often results in the slope piping on the slope in mining engineering of civil construction, and its piping phenomenon is associated with the slope of the gradient, soil cohesion, friction angle and particle size distribution, so the critical hydraulic gradient value estimate is complex for the occurring of the piping. Barja [1] said that the upwards seeping sands will reduce the effective stress, and when the effective stress lowers to zero, soil will lose its shear strength and float, so this phenomenon is called quick sand or piping, which resembles bubbles in boiling water, and the hydraulic slope gradient is the critical hydraulic gradient value at this time.

Takshashi [2] used the natural earth-rockfill dam overtopping failure to describe 3 different failures, of which one is the piping caused by seepage of the fine-grained sands in the dam. However, when the piping phenomenon is generally analyzed, the failure caused by the vertically upward bulge of the soil body will be mostly discussed, for example, Lefebvre [3]. The piping failure as a result of the slope seepage is different from the vertical used by the general analysis, and if the vertical critical hydraulic gradient is used for estimating its safety coefficient, it may be overestimated. In this study, the critical hydraulic gradient estimation formula of Barja [1] corrected by Wang [4] is used for correcting the critical hydraulic gradient estimation formula together with the empirical formula for the porosity and the coefficient of permeability. In order to discuss influences of different sized graded sands, 5 different size graded sands in this study are used for implementing the physical model experiment of the piping so as to discuss the relation between the

particle size distribution and the critical hydraulic gradient, and finally the the relation between the critical hydraulic gradient value of the soil body on the slope and the occurred piping is discussed based on the theoretical derivation, physical model experiment and numerical model analysis.

Theoretical background and analytical method

In terms of the saturated soil element on slope, considering the water pressure, normal force, drag force, soil friction and cohesive force, Wang [4] estimated the critical hydraulic gradient of the uniform particles of sand by the following equation:

$$i_c = \frac{\gamma'(1+k_0)(1+\tan\phi') + S_f + S_c - \gamma_{sat} \sin\beta}{2\gamma_w + \frac{18\mu K(1-n_e)}{D^2 n_e}} \quad (1)$$

The i_c is the critical hydraulic gradient of uniform sand; n_e is the effective porosity of the soil; μ is the fluid viscosity coefficient; D is the average particle size of the uniform particles of sand; S_c is the effective cohesion; S_f is the effective friction; γ_{sat} is the soil saturated unit weight; γ' is the unit weight of soil particles; K is the hydraulic conductivity; γ_w is the water unit weight; β is the slope angle; ϕ is the soil friction angle; k_0 is the static soil pressure coefficient. The said equation is the estimation formula of the critical hydraulic gradient of the uniform sand. The critical hydraulic gradient correlates to the hydraulic conductivity, so this study uses the Eq. 2 of the hydraulic conductivity estimated by Hazen [5] in the graded sand to correct the critical hydraulic gradient as the Eq. 3.

$$K = \frac{\gamma_w}{\mu} C D_{10}^2 \quad (2)$$

$$i_c^* = \frac{g'(1+k_0)(1+\tan f') + S_f + S_c - g_{sat} \sin b}{2g_w + 18C g_w \frac{(1-n_e)_c D_{10}^{\frac{2}{3}}}{D^{\frac{2}{3}}}} \quad (3)$$

In the above equations, i_c^* is the critical hydraulic gradient of the graded sand; C is the Hazen constant; D_{10} is the effective particle size of the graded sand. Because D_{10} and D are the particle size distribution parameters, in this study we assume its ratio is D^* (i.e. the ratio of particle size parameters, $D^* = D_{10} / D$), and uses different graded sands to conduct the physical model experiment to discuss the optimal D^* value. The physical characteristics of the 6 different graded sands (#1~#6) are listed in table 1.

Table 1 Physical characteristics of experimental sands

NO.	Gran size distributions (cm)			Specific weight	Porosity (%)	Hydraulic conductivity K (cm/sec)	Friction Angle ($^\circ$)
	D_{10}	D_{50}	D_{60}				
#1	0.027	0.043	0.047	2.65	38.40	3.00×10^{-2}	22.71
#2	0.024	0.031	0.034	2.54	37.93	9.08×10^{-3}	25.07
#3	0.019	0.025	0.026	2.49	37.23	7.56×10^{-3}	28.53
#4	0.014	0.022	0.023	2.46	35.43	6.52×10^{-3}	29.39
#5	0.009	0.016	0.018	2.41	33.42	5.76×10^{-3}	29.20
#6	0.054	0.063	0.070	2.40	37.82	8.50×10^{-3}	26.34

Physical model experiment and analytical result

As for the piping equipment used by the physical model experiment in this study, its water supply tank contains an adjustable constant-head device made of acrylic plate. This device is measured 70cm high, 15cm long and 15cm wide. The tank is 100cm (L)*15cm (W)*40cm (H). On the side bottom of the tank, there are 12 piezometer tubes. The distance between each tube is 8cm. The seepage outlet is the constant-head device measured 6cm high. The high-precision instrument is used for measuring the seepage flow at the output.

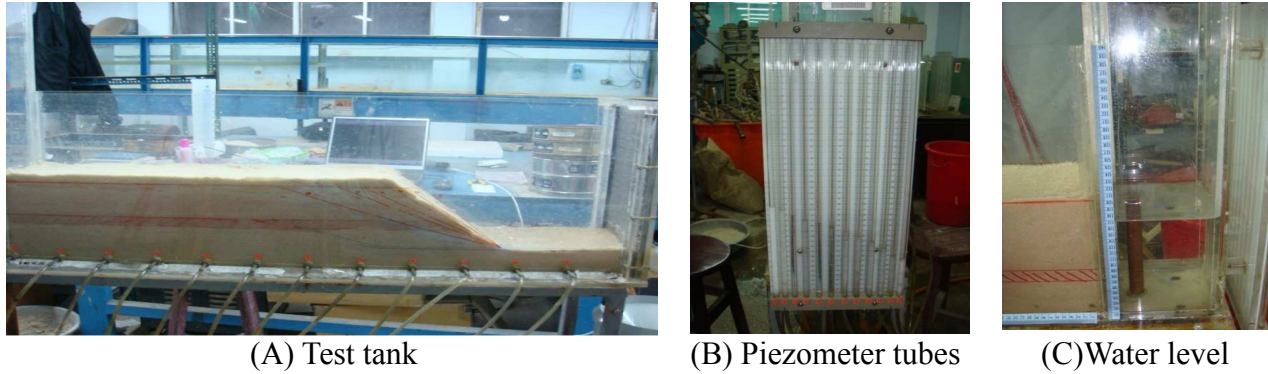


Fig. 1 Equipment for physical model experiment

Different experimental sands are put in the tank during testing. These sands are set in different slope angles (Fig. 1-A). The height of the water supply tank is adjusted from 10cm at 0.5cm each time. 30 minutes after adjusting, the water flow is stable and the slope surface is checked if the piping occurs, and the instrument is used for measuring continuously seepage flow at the outlet. Each time when the water supply height is adjusted, the hydraulic gradient is increased, so the seepage flow at the outlet also increases. When the piping phenomenon on the soil slope occurs, in addition to the occurrence of the slope deformation, the fine particulate materials flows out from the piping channel formed will increase the seepage flow abruptly. It will become stable after the collapsed slope deforms, and the seepage flow at this time will gradually become stable (Fig. 2). Table 2 shows the test data of the constant-head and the seepage flow at the outlet when the piping phenomenon occurs after different experimental sands are placed at different slope.

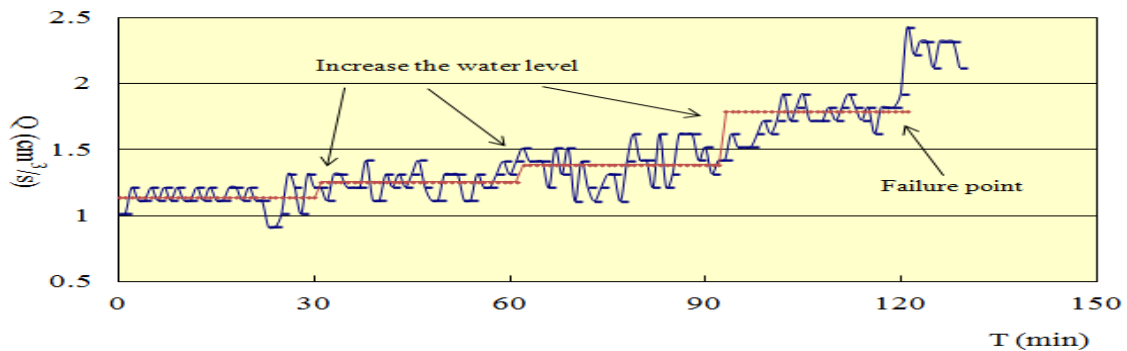


Fig. 2 Relation between outlet seepage flow and time

Because the pressure density and compaction in the course of filling sands are different before conducting the physical model experiment for the experimental sands, and the experiment fails to measure the hydraulic gradient value on the failure surface when piping occurs, this study uses GMS [7] module to establish the slope numerical model. After inputting parameters like surface elevation, hydrogeological parameter and boundary conditions, this study uses the development of the United States Army Corps of Engineers (USACE) and the FEMWATER three-dimensional simulation of groundwater flow numerical model written by Yeh [6], to simulate the slope seepage phenomenon. The flow control equation used by the FEMWATER model is derived from the Modified Richard's equation, and it is a flow control equation describing saturation and unsaturated media. Based on the water level height of the supply water flume and the outlet as well as the geometry of the experimental soil, the seepage flow measured by the piezometer tube is used for

calibrating the hydraulic conductivity coefficient of the experimental sands. After completing the parameter calibration, the velocity at each node can be obtained from the numerical simulation, and then the critical hydraulic gradient value can be calculated by using the Darcy's Law.

Table 2 Test data when slope of physical model experiment

Experimental sands		Slope occurred piping phenomenon			Experimental sands		Slope occurred piping phenomenon		
NO.	Slope ($^{\circ}$)	Water level (cm)	Failure point (cm)	Seepage (cm^3/s)	NO.	Slope ($^{\circ}$)	Water level (cm)	Failure point (cm)	Seepage (cm^3/s)
#1	30	19.0	73.6	1.818	#4	25	18.0	62.3	0.653
	45	18.0	78.1	1.789		30	18.0	75.5	0.556
	50	17.0	79.6	1.613		45	17.0	78.1	0.501
	60	16.0	79.7	1.336		50	17.0	79.6	0.400
#2	30	19.0	73.7	1.142		60	16.0	79.6	0.326
	45	18.0	78.1	0.755	#5	25	17.0	70.5	0.334
	50	17.0	79.6	0.552		30	16.0	76.9	0.215
	60	16.0	79.6	0.762		45	16.0	79.6	0.278
#3	25	20.0	62.6	0.764		50	15.0	79.6	0.263
	30	19.0	73.4	0.741		60	15.0	79.7	0.221
	45	18.0	78.1	0.654	#6	30	19.0	73.7	2.167
	50	17.0	79.2	0.586		45	18.5	79.0	1.754
	60	16.0	79.6	0.526		50	16.0	79.4	1.815
						60	16.0	79.7	1.926

Fig. 3 shows the comparison between the groundwater observation value of the soil after parameter calibration and the experiment value, and we can know from this figure that both of them are almost the same in water level. The difference caused around the slope site is mainly because of the occurrence of piping on the slope, so the water level changes around the collapsed site.

From the comparison between the hydraulic conductivity and the experiment value of the experimental sand after parameter calibration, we can know that the change in the hydraulic conductivity caused by different compactions after filling sands is not evident. From the numerical simulation, we also can know the velocity at the node of the failure slope (Fig. 3). The critical hydraulic gradient value of the piping can be obtained based on the Darcy's Law according to the hydraulic conductivity and the velocity at the node around the piping failure point after calibration in table 3.

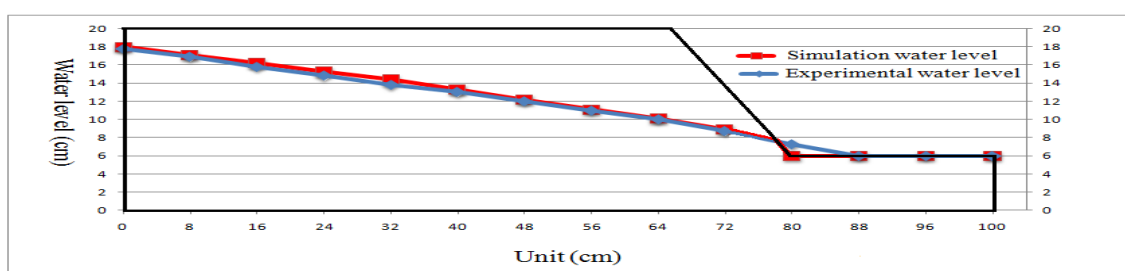


Fig. 3 Slope piping simulation and experiment water level comparison

Table 4 shows the critical hydraulic value calculated respectively according to the critical hydraulic gradient estimation formula (Eq. 1) and the numerical simulation result of the physical model experiment after calibration. From the table 4, we can know there is a difference between them. The reason why it causes such a difference is that the theoretical estimation formula applies to the uniform particles of sand only. However, the model experiment uses the graded sand, so the critical hydraulic gradient value of the graded sand can be obtained based on the Eq. 3 and the correction of the particle size parameter ratio, D^* . Table 5 shows the D^* value, ranging from 0.5 to 0.857, of each set of experimental sand at different slope angles calculated by the trial-and-error method, and we find that this correction coefficient is exactly similar to the reciprocal of the coefficient of uniformity of the graded sand. Therefore, according to the critical hydraulic gradient estimation formula on slope of the uniform particles of sand by Wang [4], the critical hydraulic gradient on slope of the graded sand is calculated as follows:

$$i_c^* = \frac{\gamma'(1+k_0)(1+\tan\phi') + S_f + S_c - \gamma_{sat} \sin\beta}{2\gamma_w + 18C\gamma_w \frac{(1-n_e)}{n_e \times C_u^2}} \quad (4)$$

Table 3 Slope piping parameter calibration and velocity at failure point

Experimental sands		Slope occurred piping phenomenon			Experimental sands		Slope occurred piping phenomenon		
No.	Slope ($^\circ$)	hydraulic conductivity (cm/sec)		Velocity at failure point (cm/sec)	No.	Slope ($^\circ$)	hydraulic conductivity (cm/sec)		Velocity at failure point (cm/sec)
		Experimental value	Parameter calibration				Experimental value	Parameter calibration	
#1	30	3.00×10^{-2}	3.012×10^{-2}	5.693×10^{-3}	#4	25	6.52×10^{-3}	6.526×10^{-3}	1.344×10^{-3}
	45		3.008×10^{-2}	5.324×10^{-3}		30		6.535×10^{-3}	1.235×10^{-3}
	50		3.013×10^{-2}	4.881×10^{-3}		45		6.537×10^{-3}	1.092×10^{-3}
	60		3.010×10^{-2}	2.860×10^{-3}		50		6.512×10^{-3}	1.022×10^{-3}
#2	30	9.08×10^{-3}	9.072×10^{-3}	1.969×10^{-3}	#5	60	5.76×10^{-3}	6.509×10^{-3}	7.090×10^{-4}
	45		9.088×10^{-3}	1.409×10^{-3}		25		5.768×10^{-3}	6.860×10^{-4}
	50		9.069×10^{-3}	1.242×10^{-3}		30		5.753×10^{-3}	5.640×10^{-4}
	60		9.085×10^{-3}	9.990×10^{-4}		45		5.772×10^{-3}	3.290×10^{-4}
#3	25	7.56×10^{-3}	7.559×10^{-3}	1.474×10^{-3}	#6	50	8.50×10^{-3}	5.749×10^{-3}	1.075×10^{-3}
	30		7.545×10^{-3}	1.456×10^{-3}		60		5.756×10^{-3}	1.117×10^{-3}
	45		7.564×10^{-3}	1.188×10^{-3}		30		8.512×10^{-3}	1.813×10^{-3}
	50		7.548×10^{-3}	1.193×10^{-3}		45		8.498×10^{-3}	1.275×10^{-3}
	60		7.562×10^{-3}	7.110×10^{-4}		50		8.504×10^{-3}	1.174×10^{-3}
						60		8.509×10^{-3}	9.620×10^{-4}

If the critical hydraulic gradient, i_c^* , on slope of the graded sand is calculated based on the aforementioned the corrected formula suggested by this study, the estimated result will be closer to the critical hydraulic gradient, i_n^* , on slope (table 4) obtained by the physical model experiment. Therefore, the subsequent sand filling project planning can use it to estimate the critical hydraulic gradient value at the occurrence of the piping phenomenon on the slope, and can use it as the reference for design and disaster prevention.

Table 4 Comparison of estimation values of critical hydraulic gradient

Experimental sands		Critical hydraulic gradient			Experimental sands		Critical hydraulic gradient		
NO.	Slope ($^\circ$)	Theoretical (i_c)	Simulation (i_n)	Theoretically corrected (i_c^*)	NO.	Slope ($^\circ$)	Theoretical (i_c)	Simulation (i_n)	Theoretically corrected (i_c^*)
#1	30	0.192	0.189	0.188	#4	25	0.211	0.206	0.209
	45	0.171	0.177	0.175		30	0.195	0.189	0.186
	50	0.166	0.162	0.163		45	0.174	0.167	0.169
	60	0.099	0.095	0.093		50	0.165	0.157	0.159
#2	30	0.221	0.217	0.215	#5	60	0.112	0.109	0.111
	45	0.164	0.155	0.153		25	0.123	0.119	0.120
	50	0.143	0.137	0.139		30	0.099	0.095	0.097
	60	0.121	0.110	0.115		45	0.064	0.057	0.062
#3	25	0.199	0.195	0.194	#6	50	0.196	0.187	0.193
	30	0.198	0.193	0.195		60	0.197	0.194	0.192
	45	0.168	0.157	0.162		30	0.221	0.216	0.219
	50	0.171	0.158	0.164		45	0.161	0.157	0.154
	60	0.098	0.094	0.096		50	0.149	0.143	0.140
						60	0.115	0.119	0.117

Table 5 Correction coefficient of critical hydraulic gradient

Experimental sands		Correction coefficient of critical hydraulic gradient		Experimental sands		Correction coefficient of critical hydraulic gradient	
NO.	Slope ($^{\circ}$)	D^*	$1/c_u$	NO.	Slope ($^{\circ}$)	D^*	$1/c_u$
#1	30	0.567	0.662	#4	25	0.759	0.762
	45	0.563	0.658		30	0.753	0.755
	50	0.562	0.654		45	0.750	0.751
	60	0.559	0.649		50	0.748	0.747
#2	30	0.592	0.738		60	0.745	0.742
	45	0.583	0.733	#5	25	0.511	0.541
	50	0.580	0.728		30	0.505	0.538
	60	0.577	0.721		45	0.500	0.533
#3	25	0.673	0.732		50	0.515	0.545
	30	0.669	0.728		60	0.519	0.552
	45	0.667	0.720	#6	30	0.857	0.777
	50	0.664	0.715		45	0.843	0.772
	60	0.662	0.711		50	0.836	0.768
					60	0.852	0.775

Conclusion

The piping caused by the slope seepage is the commonly seen failure on slope. This study uses 6 different graded sands to conduct the slop piping test in the laboratory. In the experiment, relevant physical parameters (e.g. boundary head, groundwater level, failure position and seepage volume) can be measured when the piping occurs at different slope angles. The groundwater numerical model is simulated according to the aforementioned parameters so as to obtain the hydraulic gradient value at the piping location. This value is the critical hydraulic gradient at the occurrence of the piping phenomenon. By comparing this value with the theoretical critical hydraulic gradient estimation formula of the uniform sand, we can know that some differences are mainly caused by the particle size distribution of the graded sand.

In this study, the general physical parameters of the graded sand are used for correcting the aforementioned theoretical equations. According to the corrected estimation formulae, their values are closer to the experiment values. Therefore, the subsequent sand filling project planning can use the estimation formulae of this study to calculate the critical hydraulic gradient at the occurrence of the piping phenomenon, and can use it as the reference for design and disaster prevention.

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Numerical Analysis of the Recovery Rate Influence with Stowing Roadway Mining in Daizhuang Shengjian Coal Mine

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Key words: stowing roadway; recovery ratio; numerical simulation; coal pillar width

Abstract: Daizhuang Shengjian Coal Mine has dense village above the ground. Through analyzing the process of stowing roadway mining, the author establishes a numerical calculation model about the influence of recovery rate on the mining with stowing roadway. Under the condition of fixed mining width, simulating the impact of different coal pillar width on horizontal stress of coal wall, vertical stress of coal pillar and roadway roof, at the end, according to the result of the simulation, the ratio of extraction to reservation and coal recovery ratio can be determined

1. Introduction

Daizhuang Shengjian Coal Mine is located in Huancheng Town, Weishan, Shandong, China, which is next to Weishan Lake. The mine has a 16.551 million tons coverable reserve and Huancheng town has an amount of 1.17 million tons. In order to improve the recovery of coal resources and ensure that the surface of buildings is not damaged, the technology of stowing Roadway Mining with Gangue is adopted for mining under Huancheng town.

Stowing Roadway mining is a simple crushing to deal with gangue produced under coal mine and above the ground, and then through a certain mode of transportation, the gangue can be filled in the abandoned roadway. The gangue can not only support the roof, prevent ground subsidence but also can liberate “three under” mining. Stowing roadway mining disposes a large amount of gangue which can reduce environmental pollution and damage, bring down surface subsidence and collapse, lower encroachment of farmland. Meanwhile, the coal resources under buildings are recycled and benefits of economic and social are enormous.

2. Process of stowing roadway mining

The main process of stowing roadway mining with gangue is that the gangue are transported into the top station through the crusher, and plunged into the refuse bin by turning cage, then; the gangue are delivered to the belt conveyor from under mouth feeder of refuse bin. Through the conveyor, the gangue is transported to the filling roadway, and finally they are casted to filling roadway section by the self-moving type conveyor.

Gangue filling includes the top station, turning cage, belt conveyor road, filling auxiliary roadway, filling roadway and other auxiliary roadways. The top station and machine-track combined rise are excavated in the rock and the others in the 3th upper coal seam. Belt conveyor road and filling auxiliary roadway are called machine-track combined roadway. Firstly, excavating the top station in the level of -210m, off-side of the station is linked with -210 South Roadway and haulage crosscut. The gangue warehouse is constructed in the central of the station and the right above 311railway downhill. The belt conveyor roadway is excavated in the next port 311 track

downhill and coal seams are exposed near mine field boundary. Thus, along the coal pillar protection line, filling auxiliary roadway is excavated in the coal seams which are approximate 952m [1] and close to 62-1 fault. The layout of Gangue filling roadway is shown in Figure 1.

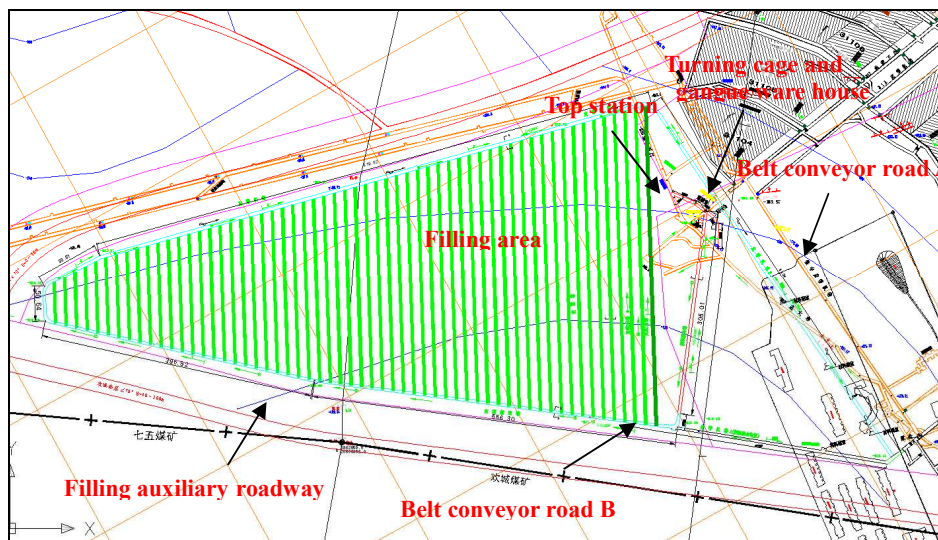


Fig. 1 Layout of gangue filling in mining area

3. Recovery rate of stowing roadway mining and numerical simulation

The original stress field changes in the stowing roadway mining. Because that the overlying strata is only supported by the isolated coal pillar, roof will be deformed and or even destructed under the action of unbalanced force fields. Then filling empty tunnel with backfill, along with the sinking of the overlying strata and the compression and the horizontal expansion of coal pillars, the backfill plays support and unconfined roles on the roof and coal pillar which improves its stress condition. Finally, the backfill interacts with the isolate coal pillar and support the overlying strata together [2]. Based on the study, recovery rate and the coal pillar width have a great impact on the stress condition of coal pillar and overlying strata. In order to grasp the impact pattern of recovery rate on three stresses, which are horizontal stress of the coal wall, vertical stress of coal pillar and roadway roof, Daizhuang Shengjian coal mine is selected as an object with the method of numerical simulation.

3.1 Selection of numerical simulation method

There are many Numerical simulation methods. Due to the combined support action of coal pillars and backfill, generally only fracture zone and curve subsidence zone appear on the overlying strata and rock mass still has a high continuity. The author chooses FLAC^{3D} software to do the simulation calculation of the stowing roadway mining.

FLAC^{3D} is an analysis application program of Three Dimensional Lagrangian which can simulate and analyze rock and soil mechanics problems of stress and deformation on tunnel excavation, slope and dam. The program which has been widely applied in the field of coal mining uses the explicit solution method to handle arbitrary nonlinear stress-strain relations.

3.2 Construction of numerical simulation model

Because coal seam inclination of Daizhuang Shengjian coal mine is small which is near horizontal seam, the coal seam is considered as horizontal seam in the numerical simulation calculation. In order to improve the speed of operation and ensure the accuracy, seven layers based on the actual geological strata are simulated and rock weight above the upper boundary of the model is regard as the stress boundary condition. Coal roof and floor are mudstone and overlying strata is 300m thickness. Due to the use of bolt-mesh supporting on the surrounding rock, the mechanical parameters are enhanced. The model is divided into the 132,000 units, 140,895 nodes. Mesh Generation is shown in Figure 2.

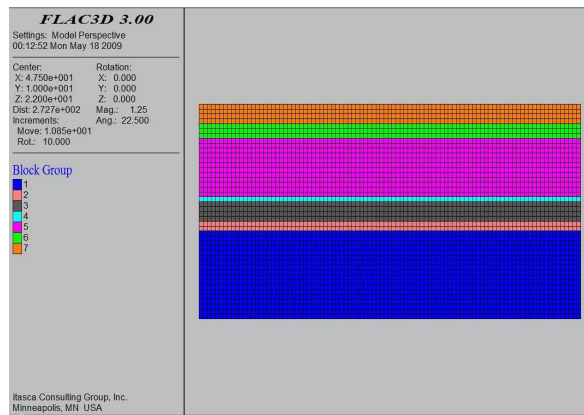


Fig. 2 Numerical analysis model Net division of stowing roadway mining recovery rate

3.3 Selection of physical and mechanical parameters of rock mass

In the model, selection of physical and mechanical parameters of each coal strata is based on the reference research and the numerical simulation is confirmed as a similar simulation. On the basis, combining with field observation data and relative theoretical research results, Using the orthogonal test method, the simulation parameters become rational and the simulation results close to truly reflect coal strata deformation and failure behavior. The physical and mechanical parameters of each coal strata which are used in the calculation are shown in Table 1.

Table 1 Physical-mechanical parameters for calculation

Lithological characters	Density (kg/m ³)	Thickness (m)	Bulk modulus (GPa)	Shear modulus (GPa)	Cohesion (MPa)	Tensile strength (MPa)	Internal frictional angle(°)
Mudstone	2200	4	32.2	10.8	6.5	0.7	50
Medium-sandstone	2700	3	25.8	8.5	3.7	0.6	28.8
Fine Sandstone	2400	12	17.2	5.7	2.7	0.5	30
Sandy Shale	1800	1	15.6	10.8	6	0.8	32.1
3th Upper Coal	1500	4	5.2	1.8	0.3	0.1	34
Siltstone	2400	2	17.6	8.8	2.1	0.6	32.1
Medium-sandstone	2700	18	25.8	8.5	3.7	0.6	28.8
Backfill	1300		1.5	0.8	0.2	0.1	43

3.4 Numerical simulation analysis on the influence of recovery rate

Because that the roadway excavation width of DaiZhuang Shengjian coal mine is 5m, a 5m × 3.5m roadway section is selected as simulation analysis. According to the actual filling ratio of 87%, the numerical simulation choose coal pillar width of 3m, 5m, 8m, 10m, 12m, 14m respectively, that means coal recovery rate of 62.5%, 50%, 38.5%, 33.3%, 29.4%, 26.3% to calculate the horizon stress condition of the coal wall, vertical stress conditions of coal pillar and roadway roof. Based on the result of numerical simulation, the variation curve between three stresses and the coal pillar width is shown in Figure 3~5.

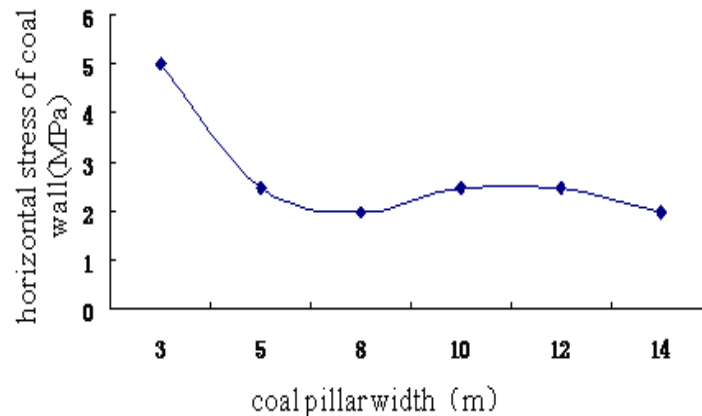


Fig. 3 Changes of horizon stress of coal wall with pillar width

From figure 3, when the coal pillar width increases from 3m to 5m, the horizontal stress of coal wall decreases rapidly. When the width is greater than 5m, the stress tends to a stable extent which is consistent with that with the mining width increasing, the horizontal stress of coal wall increases slowly and with the increasing of mining width or decreasing of coal pillar width, the stress enhances a lesser extent. Thus, the horizontal stress of coal wall gradually enhances with the increase of the recovery rate and this increase amplitude is small.

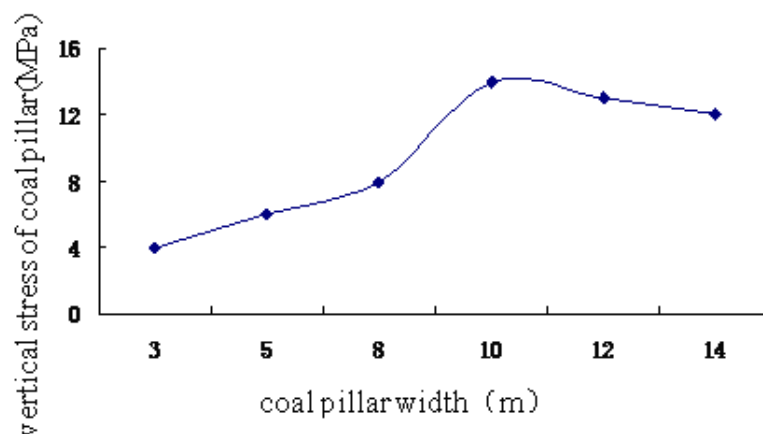


Fig.4 Changes of vertical stress of coal pillar with pillar width

Figure 4 shows that when the coal pillar width increases from 10m to 14m, the vertical stress of coal pillar decreases gradually and tends to stable. Thus, with the greater coal pillar width, the bearing loads unit area of isolated coal pillar will decrease. When the width increases to a certain degree, the stress tends to stable and will not change with pillar width.

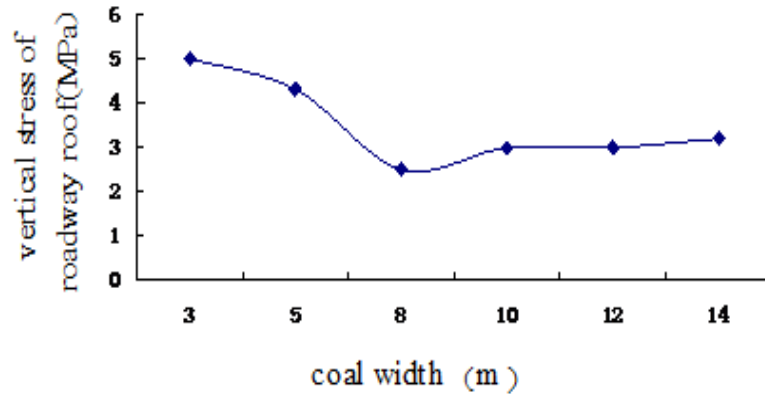


Fig.5 Changes of vertical stress of roadway roof with pillar width

Figure 5 shows that when isolated coal pillar changes from 3m to 8m, the vertical stress of roadway roof will decrease greatly. But when it increases from 10m to 14m, the vertical stress basically tends to be stable at 3.2MPa. Clearly, when the coal pillar increases to a certain extent, keeping the same mining width, the vertical stress of roadway roof becomes stable.

From the above analysis, it can be seen that with the increase of coal pillar width that is the decrease of recovery rate, the horizontal stress of coal wall and vertical stress of the roadway roof have a downward trend. When the coal pillar width increases from 10m to 14m, the decrease amplitude becomes weak and generally stable. At the same time, the vertical stress of coal pillar which firstly increases and then decreases varies greatly and also gradually becomes stable eventually. It is concluded that coal pillar width has a greater impact on the vertical stress of coal pillar and a smaller impact on the horizontal stress of coal wall and the vertical stress of roadway roof.

Therefore, in order to ensure stability of the isolated coal pillar in the process of stowing roadway mining, coal pillar width should be greater than 14m. In the early stage of stowing roadway mining with gangue, the coal pillar width of 15m is selected. After the stable filling mining in the early stage, the filling roadway will be mined in the isolated coal pillar. Ultimately, a 5m wide filling roadway and a 5m wide coal pillar are formed with 50% recovery rate.

4. Conclusion

(1) With the establish of the numerical value analysis model of the influence of recovery rate on stowing roadway mining by FLAC3D, it analyses the influence of different recovery rates on the three stresses. The changes of recovery rate are caused by the coal pillar width variations.

(2) Under the premise of ensuring the stability of coal pillars, with the recovery rate increases, the horizontal stress of coal wall and vertical stress of roadway roof increase slowly. The vertical stress of coal pillar increases by a large margin.

(3) In order to avoid the pressure influence on adjacent roadway mining, coal pillar width of 15m is prearranged in the early stage. After finishing the first filling mining cycle and forming the stability of surrounding rock, the second stowing roadway mining cycle will happen in the central of isolated coal pillars. Ultimately, the stowing mining pattern of mining 5m and leaving 5m with 50% recovery rate is formed.

5. Biography:

Li Chunsheng (1956 -), male, Wuan, Hebei Province, Senior Engineer, PH.D. Candidate in China University of Mining and Technology (Beijing), the incumbent general manager of Jingxing Coal Mining Group Corporation Ltd., Jizhong Energy Group Corporation Ltd.,

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Magnetic Separation to Recover Iron Minerals from Flotation Tailings

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Keywords: Flotation tailings; Magnetic analysis; Wet drum separator; Separation

Abstract. Large amount of surrounding rocks in Jianshui China has been discarded for many years, and the “rock” is characterized by Cu-Fe poly-metallic constituents and of low grade. A joint process of flotation and magnetic separation was proposed to process the ore. This paper introduces the test results of flotation tailings by a wet drum separator. Results show that iron concentrate assaying 60.21-68.12% Fe at a recovery of 71.9-75.32% can be obtained, when the flotation tailings assays 33.91%Fe. At the same time, a joint process has put forward to make full utilize the “rock”.

Introduction

There are about one billion tons of low grade Cu-Fe surrounding rocks left in Jianshui, Honghe municipality, Yunnan province China, as the mining operation goes on. Since the valuable minerals are of low-grade ores, and copper oxides and sulfides associate with iron minerals like magnetite, iron silicate, hematite and limonite, it was regarded as an ore that is difficult to treat and could not be utilized for many years. On the other hand, the said rocks occupy a large amount of lands, resulting in a negative impact to the surroundings.

In order to make full use of the said resource, pre-concentration of the low grade copper-bearing iron ore by dry magnetic drum is the first step to upgrade the surrounding rock (waste), where most of gangue minerals can be economically discarded as soon as possible. The principal beneficiation method for process the copper-bearing iron ores is a joint process of flotation-gravity concentration [1-3]. Through activating of copper oxide by sodium sulfide and depressing of impurities minerals like pyrite and arsenopyrite by lime, flotation process is effective in recovering the valuable copper minerals [4]. Tests in close circuit was conducted by one roughing, three-time cleaning and two-time scavenging operations, together with small amount of flotation reagents consumption, and a high-grade copper concentrate can be obtained, assaying 20.68% Cu at the recovery of 80.11%, when the raw material assays 0.79% Cu.

This paper presents the results of beneficiation of iron minerals from the flotation tailings only.

Material and Methods

A representative ore sample weighting 1200kgs taken from the surrounding rocks was transported to the laboratory by the Owner in December 20, 2011. And then the ore sample was crushed by laboratory jaw crusher and roller crusher, separately. A screen with a mesh size of 2mm is used to produce a -2mm size fraction, which is fed to a magnetic roller to enrich the iron minerals firstly, where the gangue minerals are discarded as soon as possible. A 200kg pre-enriched concentrate was used for flotation and magnetic separation tests. The sample used for magnetic separation refers to the flotation tailings, which is represented in Fig.1.

A glass tube (type DTCXG-08) that lies between two poles of C-shape electromagnet as reciprocating and swing to concentrate the magnetic minerals was used for magnetic property analysis firstly, followed by a wet drum separator (type:LX-500) to process the flotation tailings.

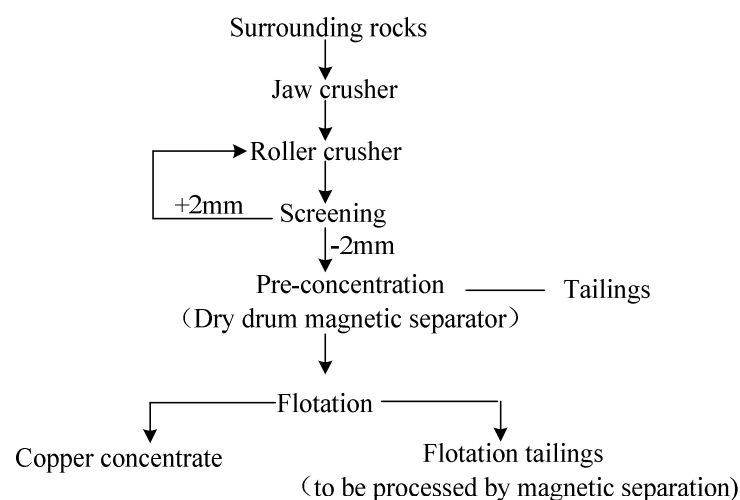


Fig.1 Flotation tailings used for magnetic separation

Results and Discussion

Sample Property

Chemical Analysis and Phase Analysis

Results of the chemical analysis of the flotation tailings are shown in Table 1. Results of iron phase analysis are shown in Table 2.

Table 1 Results of chemical analysis of the sample (flotation tailings).

Element	SiO ₂	Al ₂ O ₃	Fe	Cu	CaO	MgO	Mn	Zn	S	Au(g/t)	As	P
Content (%)	33.45	7.95	33.91	0.11	1.56	2.48	1.83	0.01	0.12	0.21	0.03	0.31

Table2 Results of iron phase analysis

Fe phase	Magnetite	Hematite and limonite	Iron silicate	Iron carbonate	Total
Content (%)	22.72	3.01	5.53	2.65	33.91
Distribution. (%)	67	8.88	16.31	7.81	100

It can be seen from Table 1, the valuable element iron is as high as 33.91%, which is expected to be recovered. However, As and P as the impurities shall be removed in concentrating the iron minerals to minimize their existence in iron concentrates. Iron phase show that the magnetite is the major phase, this part of iron minerals can easily be recovered by wet magnetic separator; but for the iron in the forms of hematite, limonite and silicates, low intensity magnetic separator will be invalid.

Magnetic Separation Tests

Magnetic Property of Flotation Tailing

Magnetic separation is often used to concentrate Fe, Mn, Ni, Ti and some nonferrous and rare metals ores. Magnetic analysis of ores is to check strong magnetic mineral content of the magnetic components in fine fractions by magnetic tube. A 50g flotation was used as a feed for magnetic tube under a magnetic field intensity of 2900Oe, at the size of 85%-200mesh, assaying 33.91% Fe. The

magnetic analysis of the flotation tailings is shown in Table 1. It can be seen from Table 1, the iron concentrate can be obtained, assaying 69.32% Fe at a recovery of 75.21. It can conclude that the sample is easy to treat by magnetic separator. As the pure magnetite contains 72.41%Fe, the obtained magnetic product contains mainly magnetite with a purity degree of 95.73.

Table 1 Results of magnetic analysis of the flotation tailings

Product	Weight (g)	Yield (%)	Grade (%Fe)	Recovery (%)
Iron concentrate	7.2	36	69.32	75.21
Tailings	12.8	64	12.86	24.79
Feed (flotation tailings)	20	100	33.19	100

Separation by Wet Drum Separator

In order to verify above results obtained by the magnetic tube, wet drum separator was introduced in the tests under the magnetic field intensity of 1300Oe and 1500Oe, respectively. Results are shown in Table 2. It can be seen from Table 2, as the magnetic field intensity goes up, the recover gets increased too, but the grade drops quickly. Therefore, the best separation result seems to be at 1500Oe. The results are useful for selecting the magnetic separator, i.e., to get a higher recovery, a higher magnetic field intensity shall be introduced.

Table 2 Results obtained by wet drum separator

Product	Yield (%)	Grade (%Fe)	Recovery (%)	Magnetic field intensity
Iron concentrate	35	68.12	71.90	1300Oe
Tailings	65	14.35	28.10	
Feed (flotation Tails.)	100	33.19	100	
Iron concentrate	35.65	68.05	73.09	1500Oe
Tailings	64.35	13.88	26.91	
Feed (flotation Tails.)	100	33.19	100	
Iron concentrate	41.52	60.21	75.32	1800Oe
Tailings	58.48	14.01	24.68	
Feed (flotation Tails.)	100	33.19	100	

Since the flotation tailings contains some impurity elements like S, P, and As, iron concentrate at 1500Oe was assayed, and the chemical analysis results are as follows: 68.05%Fe, 0.10%Cu, 2.87% SiO₂, 0.6%Al₂O₃, 0.07%P, 0.02%S and 0.002%As. According to Chinese national standards, the iron concentrate is of high quality product at a good price.

Recommended Magnetic Separation Flowsheet

Based on above magnetic separation result, a recommended flowsheet was put forward, i.e., two separators at 1300Oe and 1500Oe are suggested for roughing and scavenging separately. The full flowsheet to recover copper and iron minerals are represented in Fig.2.

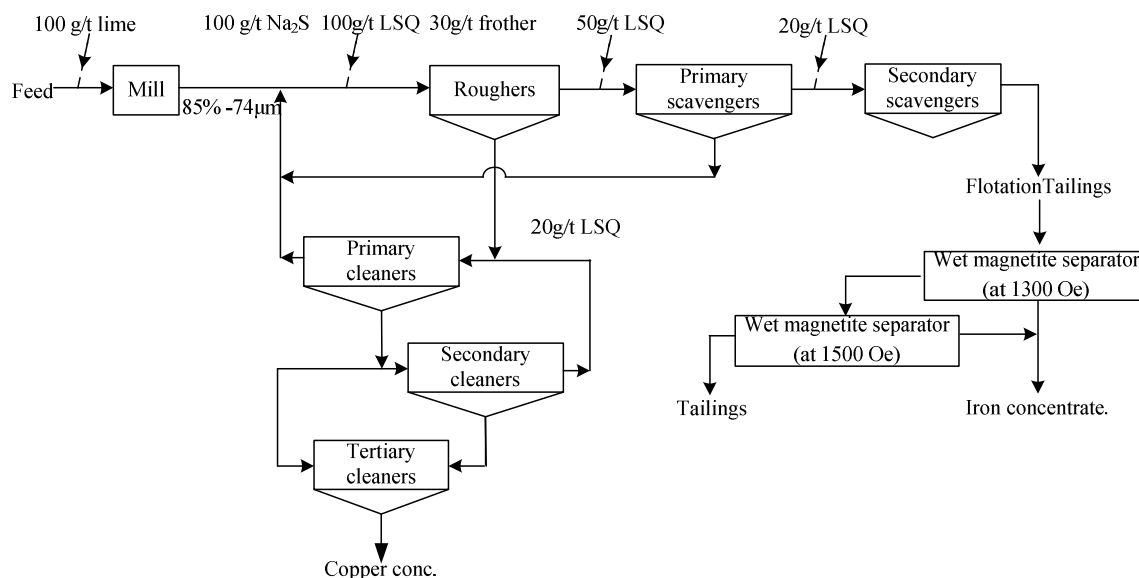


Fig.2 Recommended flowsheet

Summary

Magnetic separation is an effective method to recover iron minerals from the flotation tailings. Since the tailings contains 33.91%Fe with a grinding fineness of 85%-200mesh, further grinding is not needed. Magnetic property analysis by a magnetic tube shows that low intensity magnetic separator can effectively enrich the magnetite in the flotation tailings. Although some impurity elements S, P and As exist in the flotation tailings, they are in a small amount and exert a small effect on the quality of iron concentrate. Results obtained by wet drum separator show that high quality iron concentrate can be obtained. It should be mentioned that selecting of suitable magnetic field intensity (1300-1500Oe) for the separator plays a very important role in future operation.

Acknowledgment

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Beneficiation of a Low Grade Titanomagnetite Ore in Mining Engineering

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Keywords: low-grade titanomagnetite ore, magnetic separation, stage grinding, stage separation

Abstract: Beneficiation of a low-grade titanomagnetite ore containing 18.52%Fe and 6.65%TiO₂ was conducted by dry and wet low intensity magnetic separators. Effects of different variables, such as magnetic intensity, grinding fineness and stages of separation, were investigated in details. The ore was firstly preconcentrated by a dry low-intensity magnetic separator (DLMS) at a magnetic intensity of 2500Oe, and then ground to -0.074mm 53%, followed by a wet low-intensity magnetic separator (WLMS) to recover iron minerals. An iron concentrate assaying 49.22% Fe can be obtained at a recovery of 46.23%. The concentrate was further ground to -0.074mm 70%, followed by two stages of WLMS, and a marketable iron concentrate assaying 56.24% Fe and 9.44% TiO₂ can be obtained at the recovery of 42.89% and 20.69%, separately. Tailings assaying 6.48% TiO₂ with a recovery of 79.31% is subject to be further recovered.

Introduction

China is rich in iron resources, but majority is of low grade. According to the statistic, 94% of the iron ores need to be upgraded before entering the blast furnace smelting [1]. Generally, the ores associate with some elements, including V, Ti, Cu and S, and comprehensive utilization of above resources becomes more and more important. With the exhausting of the high-grade iron ores, the utilization of the low-grade ores challenges the mining industry both in technical and economic aspects.

In the mineralogical point, titanomagnetite consists of two main phases, i.e., magnetite (FeO·Fe₂O₃) and ilmenite (FeO·TiO₂) with some ilmenite dissolved in the magnetite matrix [2]. Due to the strong magnetism of the magnetite, the titanomagnetite exhibits magnetism to some extent. According to the results of researchers [4,5], preconcentration by DLMS prior to grinding is commonly used for concentrating the low grade magnetite ore, which can discard much surrounding rock as soon as possible, and upgrade the feed to the mills in economic way. In general, grinding and separation by stages are proved to be common and effective in processing the finely-disseminated low grade titanomagnetite ore [3, 4, 5, 6].

At the stage of primary grinding, the effective liberation between iron minerals and gangue can be basically achieved, and iron minerals can easily be enriched by magnetic separators, followed by fine grinding and wet magnetic separation by stages to get the high-quality concentrate [3]. In some cases, a joint process of magnetic separation and reverse flotation may be employed to get a high-grade iron concentrate. Firstly, the magnetite is enriched by WLMS, and then reverse flotation is conducted to upgrade the grade of concentrate by 5-6 percentage points. In reverse flotation, starch is used as depressant of iron minerals, and silicates and carbonates are separated into the float fraction by anionic collectors (fatty acid) or cationic collectors (amine) [7, 8]. But there are some limitation in use, such as complex reagents scheme, higher reagent cost for cationic collectors and higher temperature (at about 30°C) for anionic collectors.

In this paper, the basic chemical properties of the titanomagnetite ore are firstly discussed, and then beneficiation of the low-grade titanomagnetite ore by stages of grinding and concentrating is introduced in details.

Experimental and methods

The sample used in the tests was obtained from Taihe iron ore deposit in Xichang, Sichuan province, China. After crushing by laboratory jaw crushers and roll crusher, the ore was reduced to -2mm for testing and tests. According to the chemical analysis in Table 1, the sample contains 18.52% TFe, 6.65% TiO₂, little S and P with 31.26%SiO₂. The results of screening analysis show that the fine fraction (-5mm) accounts for 25.56%. Phase analysis results of iron minerals were given in Table 2, and the iron-bearing minerals are in the forms of titanomagnetite, silicates and ilmenite. Therefore, the main valuable mineral in the present research that can be recovered by low-intensity separators is titanomagnetite. Ilmenite, silicate, carbonate and sulfide will surely reported to tailings, where ilmenite can be recovered from the tailings in the future research.

Table 1 Chemical analysis of the material

Chemical composition	TFe	SFe	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	TiO ₂	S	P
Content (%)	18.52	18.31	8.91	31.26	10.52	10.64	6.33	6.65	0.24	0.13

Table 2 Phase analysis results of iron of the material.

Iron mineral	Titanomagnetite	Ilmenite	Silicate	Carbonate	Sulfide	Total
Content (%Fe)	10.20	3.02	4.40	0.60	0.30	18.52
Distribution (%)	55.08	16.30	23.76	3.24	1.62	100.00

A drum low-intensity magnetic separator (CTDG1210, Φ450×400mm) was used for the dry process. A wet low intensity magnetic separator was used for wet separation. A conical ball mill (XMQ-67 Φ240×90mm) and a set of standard Tyler screen was used for particle size analysis.

Results and discussion

Preconcentration

According to the particle size distribution of the sample, two pre-concentration methods were firstly considered below: (1) dry magnetic separation without screening, i.e., the sample is directly fed to drum magnetic separator for separation; (2) screening to -5mm and +5mm fractions and concentrating by dry- and wet- magnetic separators, respectively.

An iron concentrate assaying 23.06%Fe and 23.65% Fe were obtained at the recovery of 78.01% and 73.88% by above two methods. A higher discarding yield was achieved by DLMS. Since the main purpose of the preconcentration is to recover iron minerals maximally, so the dry magnetic separation promises to be a preferable method. Afterwards, tests on optimum magnetic intensity of preconcentration were conducted. Three variables, namely 2700Oe, 2500Oe and 2000Oe, were chosen in the tests. When the magnetic intensity was 2500Oe, an iron concentrate of 22.62% TFe and 12.17% of mFe can be obtained with a recovery of 78.07% TFe and 91.16% mFe, and a discarding yield of 33.93%. The higher magnetic intensity can obtain the same recovery and the lower iron grade in the rough concentrate, because large amount of magnetic minerals are included in gangue. However, the lower magnetic intensity will surely lead to the lower discarding yield. Therefore, the magnetic intensity at 2500Oe was appropriate in both grade and recovery considerations.

Primary grinding and concentration

The obtained rough concentrate was further ground to different fineness to liberate the iron minerals from gangue, followed by WLMS at 1650Oe. Fig.1 illustrates the effects of primary grinding fineness on recovery and grade at 1650Oe. Fig.1 shows that the grinding fineness had a significant influence on the recovery and grade of iron concentrate, i.e., the fineness increases as the recovery decreases and the grade goes up, respectively. Due to the weak magnetic attraction on finer magnetic particles, the grinding fineness at -0.074mm 53% seems to be best.

Based on above primary grinding fineness -0.074mm 53%, magnetic separation were performed to concentrate magnetic iron minerals under different magnetic intensities, shown in Fig.2. It indicates that the recovery of iron increases slightly and the grade of iron decreases a little with the increasing of magnetic intensity. It can be concluded that the magnetic intensity had a little effect on the concentration process. The optimum magnetic intensity is at 1650 Oe.

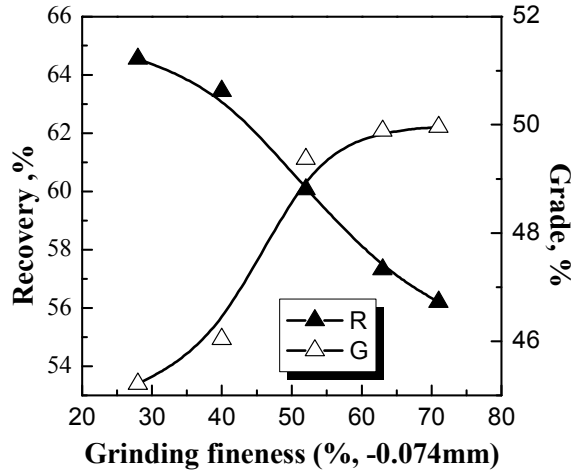


Fig.1 Effect of primary grinding fineness on the recovery and grade of iron at 1650Oe

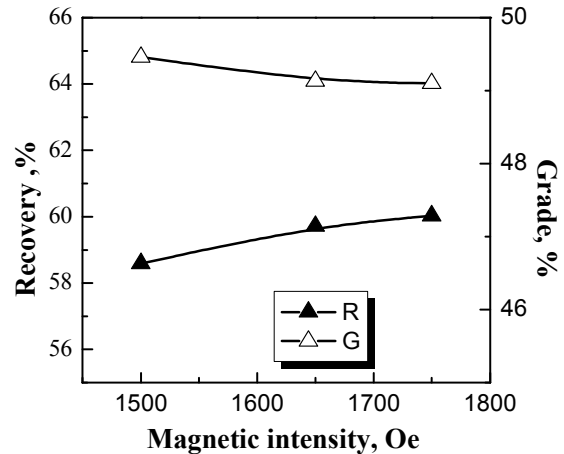


Fig.2 Effect of magnetic intensity on the recovery and grade of iron at -0.074mm 53%

Secondary grinding and concentration

The primary iron concentrate from the WLMS was further reground to achieve sufficient liberations, and then reconcentrated by WLMS in two stages (1650Oe, 1500Oe) to achieve a high-grade iron concentrate. The beneficiation results are given in Table 3. Results show that the grade and recovery of iron concentrate change hardly as the grinding fineness increases. The grade of iron concentrate can exceed 56% Fe through two times of magnetic separation at a regrinding fineness of -0.074mm 53%.

Table 4 show the results of magnetic intensity on the iron concentrate by two-stage magnetic separation. It can be seen from Table 4, there is a falling trend for the recovery of iron while the grade of concentrate increases slightly with the increasing of magnetic intensity. The magnetic intensity is suitable between 1650-1500 Oe.

Table 3 Effect of secondary grinding fineness on the recovery and grade of iron

Product	Yield (%)	Grade (%Fe)	Recovery (%)	Operation conditions	
				Magnetic intensity (Oe)	-0.074mm (%)
1-Iron conc.	81.17	56.24	92.78	1650, 1500	70
2-Iron conc.	80.33	56.25	92.55	1650, 1500	75
3-Iron conc.	80.27	56.34	92.59	1650, 1500	80
Feed	100.00	48.84	100.00	Primary iron conc.	

Table 4 Effect of the magnetic intensities on the recovery and grade of iron

Product	Yield (%)	Grade (%Fe)	Recovery (%)	Operation conditions	
				Magnetic intensity (Oe)	-0.074mm (%)
1-Iron conc.	81.80	55.92	92.99	1750, 1500	70
2-Iron conc.	81.40	56.27	92.71	1650, 1500	70
3-Iron conc.	81.03	56.52	92.34	1500, 1500	70
Feed	100.00	49.40	100.00	Primary iron conc.	

Results of the closed circuit tests

Through above research, the final flowsheet and optimum parameters were recommended in Fig.3. In the whole magnetic separation, all the middings were individually merged into the concentrate in corresponding process, and all the tailings were blended to the final tailings. After

dry magnetic preconcentration, two-stage grinding and three-stage wet magnetic separation, the beneficiation results in the closed circuit are given in Table 5. An iron concentrate of 56.24%Fe and 9.44%TiO₂ was obtained with the Fe recovery of 42.89% and TiO₂ recovery of 20.69%. There is 79.31% TiO₂ enriched in the tailings, which is to be recovered in the further research.

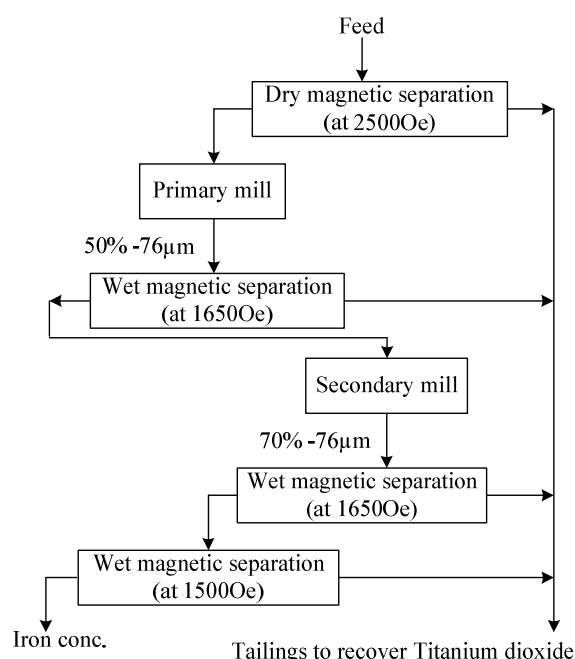


Fig.3 The closed circuit for the titanomagnetite ore

Table 5 Beneficiation results of the closed circuit tests

Product	Yield (%)	Grade (%)		Recovery (%)	
		TFe	TiO ₂	TFe	TiO ₂
Iron conc.	14.58	56.24	9.44	42.89	20.69
Tailings	85.42	12.78	6.18	57.11	79.31
Feed	100.00	19.12	6.65	100.00	100.00

Conclusions

The low-grade titanomagnetite ore subjected to this experimental study contains 18.85% TFe and 6.65% TiO₂. Iron-bearing minerals involved in the ore are titanomagnetite, ilmenite, silicate, carbonate and pyrrhotite, and titanaugite, plagioclase and olivine are the main gangue minerals. DLMS is a preferable preconcentration method with a discarding yield of 33.93%, which lowers the cost of grinding greatly. The grinding and enriching by stages are proved to be effective in concentrating the magnetite. The raw ore was primary concentrated by DLMS, and then ground and enriched by stages to recover magnetite. Finally, a marketable magnetite concentrate assaying 56.24% Fe with a recovery of 42.89% by two stages WLMS can be obtained. It should be mentioned that the tailings contains 6.18%TiO₂ accounting for 79.31% of the total, which is expected to be recovered in the further.

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